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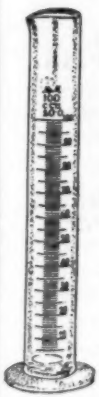

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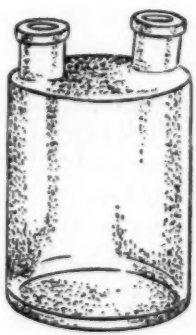

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[Jour. Indian Chem. Soc., Vol. 33, No. 9, 1956]

ABSORPTION AND FLUORESCENCE SPECTRA OF FLAVONES

By S. K. K. Jatkar and B. N. Mattoo

Absorption and fluorescence spectra of 4′-methoxyflavones with methyl and benzoyl substitutions and 4′-benzyloxyflavones with methyl and methoxy substitutions are reported and discussed.

Additional resonance due to a 4′-methoxy group in flavones results in a red-shift of the flavone spectrum. Introduction of methyl groups produces a slight bathochromic effect. Benzoyl substitution in 6-position increases conjugation to a large extent, and the possibility of additional resonance causes a radical change in the spectrum. The behaviour of 4′-benzyloxy substitution is not very much different from a 4′-methoxy, except in the high-frequency region.

Introduction of methyl groups or replacement of 4′-methoxy by 4′-benzyloxy increases the fluorescence efficiency slightly. 6-Benzoyl group shifts the fluorescence maximum to red, and causes a sharp fall in efficiency. A very large increase in efficiency by the introduction of 6-Me, 3′-OMe or 7 :3′-dimethoxy groups in 4′-benzyloxyflavone is observed.

A solvent effect in the fluorescence of flavones (not 3-OH derivatives, *i.e.* flavonols) has been observed in as much as the quantum efficiency increases considerably when the proportion of water in the EtOH-water solvent pair is increased. The effect is observable by qualitative methods and may prove of importance in identification of flavones (flavonols and isomeric benzylidene-coumaranones do not behave in this manner).

Earlier work on the absorption spectra of flavones is that of the Japanese workers (Shibata, *Acta Phytochim.*, 1922, **1**, 95; Hattori, *ibid.*, 1932, **6**, 131; Hayashi, *ibid.*, 1935, **8**, 179; 1936, **9**, 1) who have shown that this series is characterised by two bands at 2,500 and 3,000Å. Skarzyn'ski (*Biochem. Z.*, 1939, **301**, 150) studied the absorption spectra of a number of flavones in the light of their chemical constitution. According to him, the absorption of flavones depends on the presence of benzopyrone.

Aronoff (*J. Org. Chem.*, 1940, **5**, 561) showed that neither the phenyl group of flavone, as supposed by Shibata (*loc. cit.*), nor the benzo-γ-pyrone, as supposed by Skarzyn'ski (*loc. cit.*) was responsible for the flavone spectra. According to him, an oxygen in the phenone is involved which is capable of *ortho-para* resonance. Owing to restriction of the normal resonance of the pyrilium nucleus by a ketonic oxygen, the additional resonances caused by substitution follow a path through *this* oxygen, resulting in a shift of one band of the spectrum to the red (e. g., 4′-, 7-, 2′-OH substitutions).

Other work on absorption spectra of flavones includes such data for a number of polyhydroxy flavones and their methyl ethers, mostly naturally occurring substances (cf. Marchlewski and Skarzyn'ski, *Biochem. Z.*, 1938, **297**, 56; Briggs and Locker, *J. Chem. Soc.*, 1949, 2157; 1951, 3131). Mansfield *et al.* (*Nature*, 1953, **172**, 23) have utilised the ultraviolet spectra of the ions of hydroxyflavones as a means of their identification.

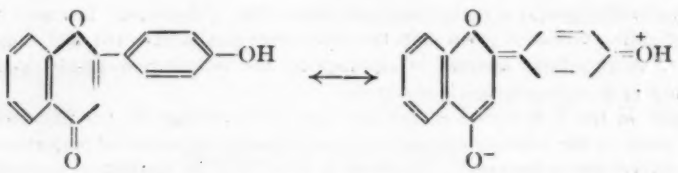
Study of fluorescence spectra of flavones has not been so far reported. Qualitative study of the exhibition of fluorescence in relation to chemical constitution has been made by Seshadri and his co-workers (*Proc. Ind. Acad. Sci.*, 1940, **12A**, 375; 1951, **34A**, 319).

Their study includes visual examination of the fluorescence, excited by daylight. No regard was taken of the exciting radiation, nor the concentration at which the solutions were viewed. As in chromones, these authors found concentrated H_2SO_4 as the medium in which flavones exhibited visible fluorescence. Pyrone double bond is found essential for fluorescence ; flavanones do not fluoresce.

In the present work the absorption and fluorescence spectra of flavones have been discussed ; the data are shown in Figs. 1-4.

Absorption

The substitution in 4′-position in flavone by an OH group causes a bathochromic shift of the long-wave band. According to Aronoff (*loc. cit.*) this is due to the following additional resonance :

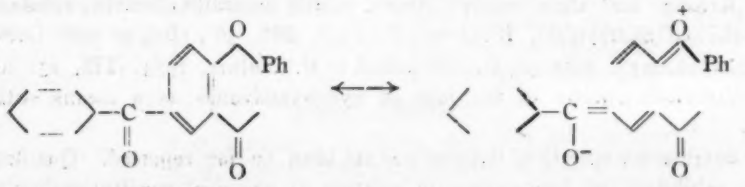


As similar resonance is possible with 4′-OCH_3- and 4′-$OCH_2\phi$-flavones, we have observed a similar shift towards the red.

4′-Methoxyflavone has a broad and intense band at 317 mμ (oscillator strength 0.605) with $\epsilon = 24{,}100$, and two other bands at 253.5 mμ and 221 mμ with $\epsilon = 12{,}800$ and 19,670 respectively. The spectra of 4′-methoxyflavone (and its Me derivatives) in neutral, $10^{-4}N$ alkaline and $10^{-4}N$ acidic media show no remarkable variation, especially in the longest wave-band, but there is a slight decrease in absorption in acid and alkaline media, which is more prominent in the 253 mμ band. This is now obviously not due to any ionisation, but, as found by Gibbs (*J. Amer. Chem. Soc.*, 1930, **52**, 4895) too, there is a tendency to form pyronium salts.

Methyl groups in 6- and 8- positions of 4′-methoxyflavone produce a slight bathochromic shift, perhaps hyperconjugative in character. The integrated absorption also increases on introduction of these methyl groups. The oscillator strengths of the 320mμ bands of 6- and 8- methyl derivatives are 0.62 and 0.61 as compared to 0.605, when there is no alkyl substitution.

Introduction of a benzoyl group at 6- position, which basically changes the character of the resonance, produces radical changes in absorption (see Fig. 3).



The integrated absorption, $\int \epsilon d\nu$, for 6-benzoyl derivative is 112.0 as compared to 74.5, when this substitution is absent.

FIG. 1

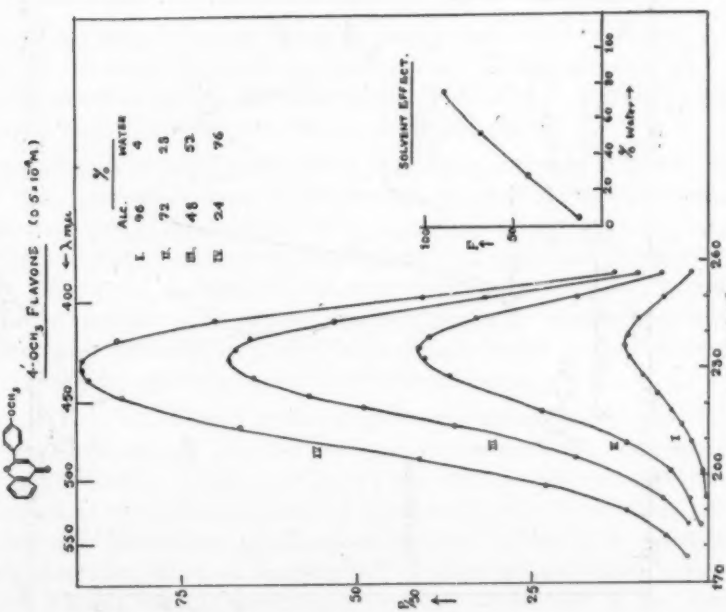
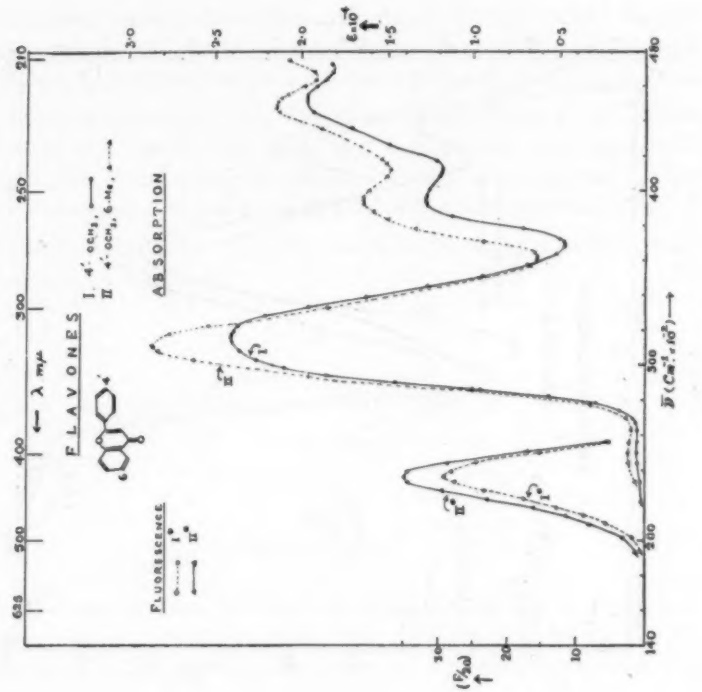

4'-OCH3 FLAVONE (0·5×10⁻⁴M)
% WATER
ALC. 96 4
I. 72 28
II. 48 52
III. 24 76
SOLVENT EFFECT.
% WATER →
λ mμ
ν̄ (cm⁻¹×10⁻³)

FIG. 2


FLAVONES
I. 4'-OCH3,
II 4'-OCH3, 6-Me,
ABSORPTION
FLUORESCENCE
λ mμ
ν̄ (cm⁻¹×10⁻³)

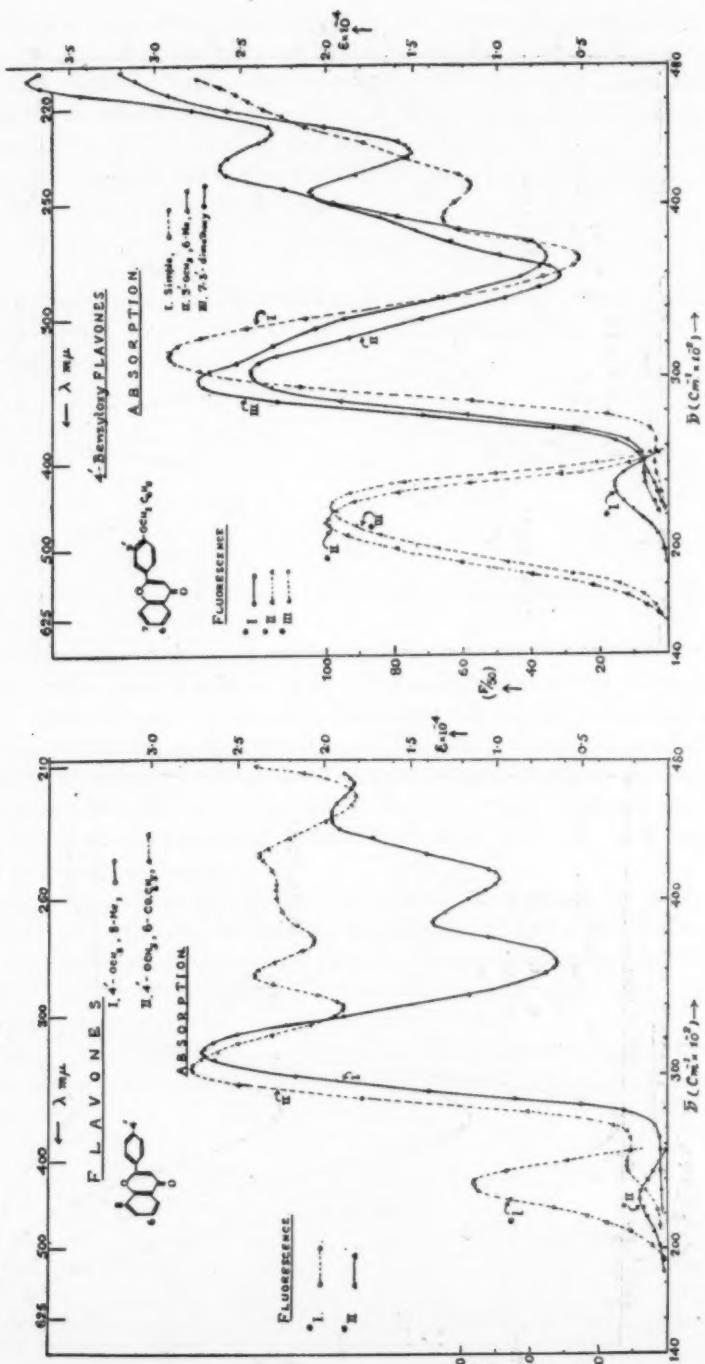

FLAVONES
I. 4'-OCH3, 5-OH, ⟶
II. 4'-OCH3, 6-CH2CH3, ⟶
ABSORPTION
FLUORESCENCE
I. ⟶
II. ⟶
λ mμ
ε·10⁻⁴
F (Cm² · 10²) ⟶
(F/F20) ⟶

FIG. 3

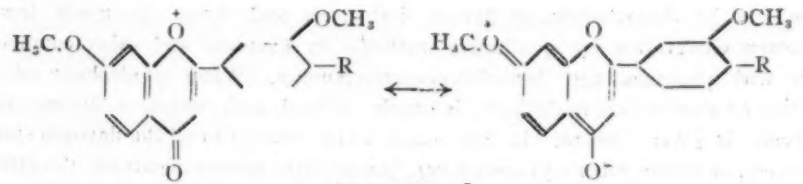
4'-Benzyloxy-FLAVONES
ABSORPTION
I. Simple, ⟶
II. 5-OCH3, 6-Me, ⟶
III. 7,5'-dimethoxy ⟶
FLUORESCENCE
I ⟶
II ⟶
III ⟶
λ mμ
ε·10⁻⁴
F (Cm² · 10²) ⟶
(F/F20) ⟶

FIG. 4

Except for minor changes, the replacement of a $-OCH_3$ by $-OCH_2\phi$ does not change the nature of spectrum. However, the phenyl group does contribute to the total absorption as $-O-CH_2-\phi$ is incapable of complete insulation from the rest of the molecule.

6-Me-3′-OCH_3 substitution in 4′-benzyloxyflavone causes a bathochromic shift ($\Delta\lambda = 10.5$ mμ) in the longest wave-band, and an increase in $\int \varepsilon d\nu$ (from 86.0 to 93.0), but retains the nature of the spectrum, because $-OCH_3$ in 3′-position cannot produce any additional resonance, as it does when in *para* (4′-) or *ortho* (2′-) position.

7 : 3′-Dimethoxy substitution, however, makes a difference ; 7-OCH_3 group can give rise to the resonance of the type :



[R = $OCH_2\phi$]

Now there appears an additional (unresolved) band indicated by a shoulder at 305mμ in addition to maxima at 336 and 237.5mμ. The appearance of an intense short-wave band at 212mμ is also a deviation from the other two benzyloxyflavones described above. $\int \varepsilon d\nu$ now increases to 108.3.

Fluorescence

The fact that simple flavone fluoresces shows that a free hydroxyl is, unlike chromones, not necessary to make the compound exhibit fluorescence. The 2-phenyl substitution in chromone nucleus increases resonance, so much so that even without a hydroxyl in a favourable position, the flavones are fluorescent.

4′-Methoxyflavone is found to exhibit a blue-violet emission excited by hydrogen discharge. The fluorescence band has maximum at 425mμ and extends roughly from 380mμ to 520mμ. Methyl substitution at 6- or 8- position does not make any significant difference. Thus, 6- and 8- methyl derivatives have λ^F_{max} at 425 and 423mμ respectively and relative $\int F d\nu$ equal to 1170 and 900 respectively, as compared to relative $\int F d\nu$ of 960 for 4′-methoxyflavone. The higher total fluorencence of 6-methyl derivative does not indicate a higher yield because of its correspondingly higher integrated absorption ; it has roughly the same efficiency as that of 4′-methoxyflavone.

Replacement of 4′-OCH_3 by 4′-benzyloxy makes only a slight increase (~20%) in efficiency, while the λ_{max} of the fluorescence band does not shift. Intr oduction of 6-methyl, 3′-methoxy or 7 : 3′-dimethoxy groups in 4 -benzyloxyflavone, however, makes a great difference, in as much as the efficiency increases considerably (roughly 7-8 times), and also a shift in λ^F_{max} to 465mμ and 445mμ respectively. There is a red-shift of the longest-wave absorption band on introduction of these groups which may partly be responsible for a similar effect in fluorescence spectrum. The effect of 7 : 3′-dimethoxy

substitution can be expected because of the increase in resonance due to 7-OCH_3, but that of 6-Me-3′-OCH_3 substitution, which is as significant as the former, is not clear at present.

Introduction of a benzoyl group in 6-position of 4′-methoxyflavone causes a sharp fall in efficiency ($\int \epsilon d\nu$ and relative $\int F d\nu$ for 4′-methoxyflavone and its 6-benzoyl derivative being 74.5; 960 and 112.0; 170 respectively). A red-shift in absorption is also apparent in the fluorescence spectrum (λ^F_{max} now being at 440mμ). The decrease in efficiency is possibly due to hampering of the normal electron drift from anionoid oxygen at 1 to cationoid oxygen at 4-position. The 'inner-filter' effect due to higher absorption in the blue region will also account for a slight fall in efficiency.

A solvent effect, which may be of importance in identification of flavones, is found to be characteristic of flavone derivatives and absent (or much less so as to escape observation by qualitative methods) in flavonols and other compounds isomeric with flavones, e.g. benzylidene-coumaranones. When an alcoholic solution (exhibiting no fluorescence in daylight) is largely diluted with water, a distinct violet fluorescence is given rise to. It was found to be common to all the flavones studied here (expect, of course, 6-benzoyl derivative). Quantitative measurements for 4′-methoxyflavone showed that the F_{max} as well as $\int F d\nu$ increased almost linearly with increase in the proportion of water in EtOH-water solvent pair (Table I).

TABLE I

% Water	...	4	28	52	76
λ^F_{max} (mμ)	...	425	425	430	432
F_{max}	...	585	2,050	3,395	4,455
$\int F d\nu$	...	960	3,625	6,510	10,025

There is, however, no significant change in absorption spectrum when changing the proportion of water in the solvent. Why the higher dielectric constant of water causes a large increase in quantum efficiency of the emission in case of flavones and not flavonols or other isomers should make an interesting study. The slight red-shift in fluorescence maximum with higher dielectric constant of the solvent is in conformity with the results reported by previous workers (cf. Ganguly, *Science & Culture*, 1946, **12**, 114).

EXPERIMENTAL

Measurements of the ultraviolet absorption spectra and fluorescence spectra were made in the manner as described in a previous paper (this *Journal*, 1956, **33**, 604). Measurements of absorption were made at a concentration of $0.5 \times 10^{-4} M$ in neutral, $10^{-4}N$-HCl and $10^{-4}N$-KOH media. The solvent was aqueous alcohol (87%). Fluorescence spectra were taken in alcoholic (96%) solution at the same molar concentration. Alcohol was purified according to Harris (*J. Amer. Chem. Soc.*, 1933, **55**, 1940) and Clow and Pearson (*Nature*, 1939, **144**, 208). 1 cm (± 0.001 cm) cells were used for

taking absorption spectra; the readings were taken at 10Å intervals at maxima and minima and these were located to 5Å, whenever possible. The accuracy in ε_{max} values is within ± 1% and $\bar{\nu}_{max}$ values are correct to ± 0.2%. The errors in $^{\nu}$alues of ε_{max} due to the different fluorescing capacities of the various compounds studied are intrinsic in these measurements.

Integrated absorption (between the limits 2,100 Å and 5,000Å) and fluorescence have been calculated from the areas of the respective spectral curves, measured planimetrically. In comparing fluorescence efficiencies qualitatively, no cognizance has been taken of the spectral distribution in the exciting radiation. One is not unjustified in doing so, as long as the absorption spectra are very similar in nature. The compounds used were pure as judged by their m.p.'s.

Thanks are due to Dr. M. G. Marathey for making the compounds available for the present study.

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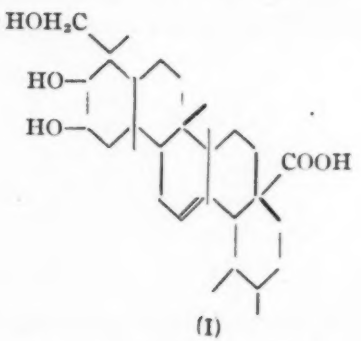
CONSTITUENTS OF *CENTALLA ASIATICA*. PART II. STRUCTURE OF THE TRITERPENE ACIDS

By S. C. Bhattacharyya

The triterpene acids of *Centalla asiatica* from Ceylon have been critically examined and structures assigned to them.

In Part I of this series (this *Journal*, 1956, **33**, 579), the isolation of three polyhydroxy triterpenic acids—centic acid ($C_{30}H_{48}O_5$), centoic acid ($C_{30}H_{48}O_6$) and centellic acid ($C_{30}H_{48}O_6$)— from the Ceylonese variety of *C. asiatica* has been described. The structures of these acids are now being discussed. The acids have been found to be closely related to the typical triterpenic acids like oleanolic acid. Recently, the structure of asiatic acid, the triterpenic aglycone of the glycoside, asiaticoside, isolated from the Madagaskar variety of *C. asiatica*, has been elucidated (Polonsky, *Bull. soc. chim.*, 1953, 173). It belongs to the α-amyrin group and is represented by (I).



(I)

Since asiatic acid from *C. asiatica* from Madagaskar belongs to the α-amyrin group, it has been provisionally assumed that the three acids from the Ceylonese variety of the plant would also belong to the same fundamental group.

Centoic Acid.—With diazomethane it formed a methyl ester ($C_{31}H_{50}O_6$) which could not be hydrolysed by prolonged treatment with acid or alkali, thus revealing the tertiary nature of the carboxyl group. The acid did not show any U.V. absorption and it failed to react with any carbonyl reagent. The absence of any alkoxyl group in it was confirmed by Zeisel's method. In alcoholic solution centoic acid and its derivatives developed colour reaction with tetranitromethane, indicating the presence of unsaturation. As in the case of other triterpenes, the double bond was, however, inert and could not be hydrogenated in presence of Adams' catalyst. It reacted with bromine to form a monobromolactone, revealing that, as in the case of many other triterpenic acids, the double bond in this case also was in γδ-position to the carboxyl group (Winterstein and Hammerle, *Z. physiol. Chem.*, 1931, **199**, 56, 64, 74; Haworth,

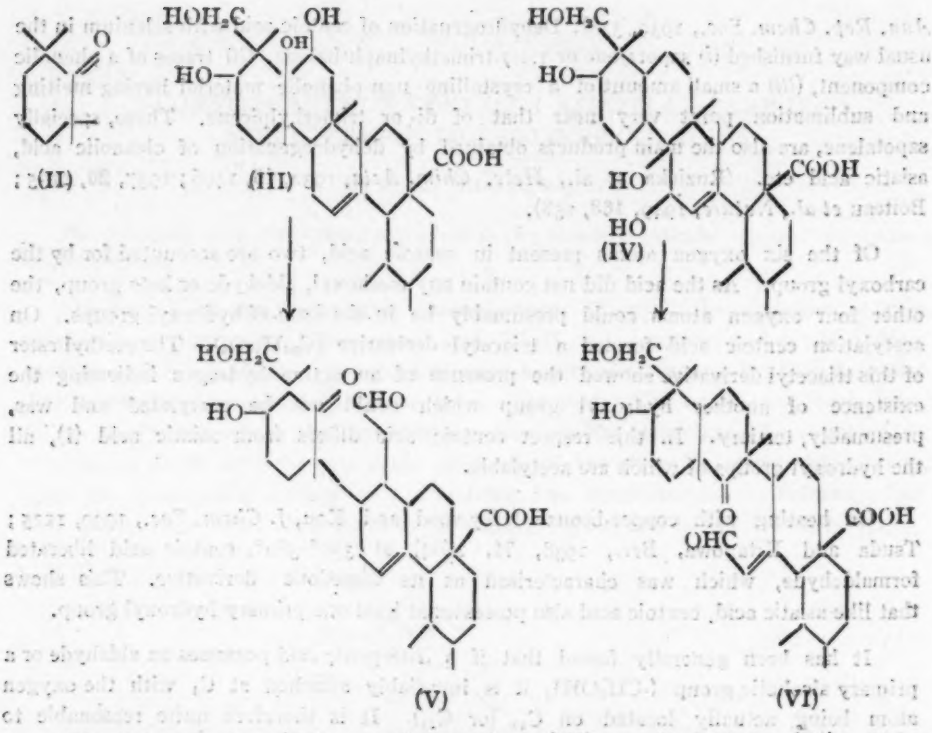
Ann. Rep. Chem. Soc., 1939, 338). Dehydrogenation of centoic acid with selenium in the usual way furnished (*i*) sapotalene or 1:2:7-trimethylnaphthalene, (*ii*) traces of a phenolic component, (*iii*) a small amount of a crystalline non-phenolic material having melting and sublimation point very near that of di- or trimethylpicene. These, specially sapotalene, are also the main products obtained by dehydrogenation of oleanolic acid, asiatic acid etc. (Ruzicka *et al.*, *Helv. Chim. Acta*, 1932, **15**, 1496; 1937, **20**, 1155; Boiteau *et al.*, *Nature*, 1949, **163**, 258).

Of the six oxygen atoms present in centoic acid, two are accounted for by the carboxyl group. As the acid did not contain any methoxyl, aldehyde or keto group, the other four oxygen atoms could presumably be in the form of hydroxyl groups. On acetylation centoic acid formed a triacetyl derivative ($C_{36}H_{54}O_9$). The methyl ester of this triacetyl derivative showed the presence of an active hydrogen indicating the existence of another hydroxyl group which could not be acetylated and was, presumably, tertiary. In this respect centoic acid differs from asiatic acid (I), all the hydroxyl groups of which are acetylable.

On heating with copper-bronze (Heywood and Kon, *J. Chem. Soc.*, 1939, 1125; Tsuda and Kitagowa, *Ber.*, 1938, **71**, 1604) at 350°-380°, centoic acid liberated formaldehyde, which was characterised as its dimedone derivative. This shows that like asiatic acid, centoic acid also possesses at least one primary hydroxyl group.

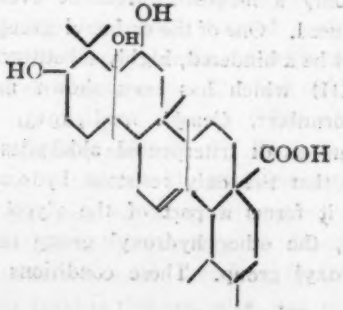
It has been generally found that if a triterpenic acid possesses an aldehyde or a primary alcoholic group ($-CH_2OH$), it is invariably attached at C_4 with the oxygen atom being actually located on C_{23} (or C_{24}). It is therefore quite reasonable to assume that centoic acid will be no exception, and that the primary alcoholic group in it is also attached at C_4, though we have no direct evidence.

Centoic acid consumed one mole of periodate. During this reaction no formaldehyde or acetone was eliminated. Like the parent compound, the resultant scission product also contained 30 carbon atoms ($C_{30}H_{46}O_6$). The glycol linkage in centoic acid therefore does not exist as a side-chain but is a component part of the ring structure itself. This scission product contained at least one aldehyde group as it reduced Fehling's solution and also gave characteristic colour reactions with *o*-dianisidine, benzidine etc. It formed only a monosemicarbazone even when an excess of semicarbazide hydrochloride was used. One of the carbonyl groups in the scission product is therefore inert and must be a hindered, highly substituted keto group as in 2:2:6.6-tretamethyl*cyclo*hexanone (II) which has been shown not to form any carbonyl derivatives (Haller and Cornubert, *Compt. rend.*, 1913, **156**, 1199). This cannot possibly be an aldehydic group, as all triterpenoid aldehydes do form semicarbazones. It is therefore quite clear that the only resistant hydroxyl group present in centoic acid is a tertiary one, and it forms a part of the glycol linkage. As the scission product is a keto-aldehyde, the other hydroxyl group present in the glycol linkage must be a secondary hydroxyl group. These conditions can be satisfied only by (III) and (IV).



On glycol-cleavage (IV), as distinct from (III), would lead to (VI) with an αβ-olefinic aldehyde group. Since the scission product obtained from centoic acid did not show any strong ultraviolet absorption specific for an $\alpha\beta$-unsaturated carbonylic system, structure (IV) was ruled out. Centoic acid therefore is represented by (III).

Centic Acid.—Analysis and equivalent weight suggest the molecular formula of centic acid as $C_{30}H_{48}O_5$. It contains one oxygen atom less than centoic acid. Like centoic acid it also contains an α-glycol linkage, which from analogy should be located in the same position in the ring system. Centic acid therefore has been represented by (VII).



(VII)

Centellic Acid.—Details about the molecular formula of centellic acid ($C_{30}H_{48}O_6$) has been described earlier (*loc. cit.*). Like centoic acid it also showed the presence of a primary hydroxyl group (copper-bronze test), an α-glycol linkage, the latter being located in the same position in the ring system. Centellic acid is, probably, a structural isomer of centoic acid, differing only in the configuration of the glycol linkage. In that case the periodate scission product of the two acids should be identical. But as both the products were amorphous and without having any sharp melting point, a reliable comparison was difficult.

EXPERIMENTAL

Unless otherwise stated, samples were dried to a constant weight at about 100°-110°/1-2 mm. before examination.

Triacetylcentoic Acid.—The acid (1 g.), anhydrous sodium acetate (0.5 g.), acetic acid (5 c.c.) and acetic anhydride (10 c.c.) were refluxed for 2 to 3 hours. The product was then decomposed in the usual way, extracted with chloroform, purified by precipitating from acetic acid solution with water, and dried. It softened at 160° and formed a glass at 166-69°; $[\alpha]_D^{30}$, +5°.1 (c=0.834%, alcohol). (Found: C, 68.30; H, 8.26; equiv., 633.7. $C_{36}H_{54}O_9$ requires C, 68.55; H, 8.63 per cent. Equiv., 630.80).

Triacetylmethyl ester was prepared by the reaction of the triacetyl derivative and diazomethane in ethereal solution and purified by precipitation from acetic acid solution with water, and dried. It softened at 140° and formed a glass at 160°; $[\alpha]_D^{30}$, +7°.0 (c=1.142%, alcohol). (Found: C, 69.05; H, 9.06; active H, 0.18 $C_{37}H_{56}O_9$ requires C, 68.90; H, 0.76; active H, 0.183 per cent). An identical acetylated methyl ester could also be prepared by acetylating the methyl ester in the usual way with sodium acetate and acetic anhydride.

Monobromolactone of Centoic Acid.—To the acid (0.5 g.), dissolved in methanol (50 c.c.), bromine (0.5 g.), dissolved in methanol (10 c.c.), was added and the mixture set aside for 24 hours. After removal of the solvent the residue was taken up in chloroform and washed successively with bicarbonate, water, and dried. After removal of the chloroform the residue was dissolved in alcohol and precipitated by addition of water. The product indicated a strong Beilstein test for halogen and was insoluble in caustic soda or potash, thus indicating its lactonic nature. (Found: Br, 13.41. $C_{30}H_{47}O_6Br$ requires Br, 13.7 per cent).

Dehydrogenation of Centoic Acid.—The acid (4·5 g.) was intimately mixed with selenium (6 g.) and then heated in a long-necked flask (2½ ft.) for 48 hours at 350°-400°. The contents of the flask were then powderd very thoroughly and exhaustively extracted with ether in a Soxhlet apparatus for 24 hours and then with dioxane for another 24 hours. The combined extract after removal of the solvent was once totally distilled at 10^{-3} mm. and then fractionated from a retort at 10^{-3} mm. into four fractions at different bath temperatures: (*i*) up to 90°, (*ii*) 90°-115°, (*iii*) 115°-150° and (*iv*) 150°-250°.

Fraction (*i*) contained traces of a phenol and gave a colour reaction with diazonium chloride. The non-phenolic portion and also the fraction (*ii*) formed a reddish yellow picrate, which after three crystallisations from alcohol melted at 127°, identical with sapotalene picrate, m.p. 128°. Fractions (*iii*) and (*iv*) were very small in quantity. After chromotography and micro-vacuum sublimation (bath temperature 250°-305°/10^{-3} mm) a product of m.p. 298° was obtained, sublimation temperature and melting point of which compared with those of 1:8-dimethylpicene, m.p. 305-306° (corr.) and 1:7:8-trimethylpicene, m.p. 309-310°.

Detection of Primary Alcoholic Group.—An intimate mixture of centoic acid (1 g.) and copper-bronze (25 g.) was taken in an adequate apparatus, the side arm of which was dipped in a nearly saturated aqueous solution of dimedone. The flask was heated at 350°-380° in a metal bath while a slow current of nitrogen was passed through it. The dimedone derivative, which started appearing after 15 minutes, was collected after two hours and crystallised from dilute alcohol; m.p. and mixed m.p. 189°.

Periodate Scission Product of Centoic Acid.—The acid (1.48 g.) was oxidised with periodate (65 c.c., 0.2641 *M*) following the same procedure as described for the evaluation of the glycol linkage (vide Part I, *loc. cit.*). The scission product was filtered, washed with water and then purified by precipitating with water from alcohol or acetic acid, filtered, washed with water and dried; yield 1.3 g. On a preheated (150°) block it softened at 185° and decomposed at 202°-205° with frothing; $[\alpha]_D^{19}$, +91°.6 (pyridine, c = 1.27%). (Found: C, 71.45; H, 9.10; equiv., 502.0. $C_{30}H_{46}O_6$ requires C, 71.68; H, 9.22 per cent. Equiv., 502.7).

The product did not show any specific U.V. absorption. The monosemicarbazone of the above scission product was prepared in the usual way. It was finally obtained as a micro-crystalline powder by cooling from a dilute alcoholic solution. In a preheated block it shrank at about 200° and decomposed with frothing at 220°-225°. (Found: N, 7.36. $C_{31}H_{49}O_6N_3$ requires N, 7.51 per cent).

Centellic Acid.—The acid, as expected, could not be hydrogenated and showed no ultraviolet absorption. The methyl ester was resistant towards acid and alkali.

Acetylation of Centellic Acid.—Acetylation was carried out as in the case of centoic acid. In this case the extent of acetylation depended on the duration of reaction, as indicated by the periodical determination of the equivalent weight: after one hour, approximately 680; after 2 hours, 700; after 6 hours, 715. Longer heating appeared to induce side reaction. (Found: C, 67.0; H, 8.15; equiv., 710.0. Triacetyl derivative $C_{36}H_{54}O_9$ requires C, 68.54; H, 8.63; tetracetyl derivative $C_{38}H_{56}O_{10}$ requires C, 67.83; H, 8.39 per cent). For the same sample $[\alpha]_D^{19} = -7°.28$ (alcohol, c = 1.51%).

Primary hydroxyl group in centellic acid was detected by employing the same procedure as in the case of centoic acid.

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THE BEHAVIOUR OF MOLYBDENUM ON CATHODIC POLARISATION WITH REFERENCE TO THE EFFECT OF ANIONS ON ITS HYDROGEN OVERPOTENTIAL

By H. Khalifa and I. M. Issa

The overpotential of hydrogen is measured in pure HCl solution of concentration ranging from 5.91 – 0.003*N*. Within this concentration range and at current densities = $1 \times 10^{-5} - 1.8 \times 10^{-4}$ amps./cm^2 the Tafel-line slope amounts to 0.06, which suggests a dual electrochemical-catalytic mechanism. At lower acid concentrations than 0.1 *N* and at higher currents than 1.8×10^{-4}, the Tafel-line slope increases continuously up to 0.116 in 0.003 *N*-HCl. Borate and nitrate ions possess a pronounced effect on the slope of the Tafel lines, but the effect of phthalate is small.

In a previous investigation involving a study on the behaviour of chromium in the course of cathodic and anodic polarisation (Issa, Ammar and Khalifa, *J. Phys. Chem.*, 1955, **59**, 492), we observed that the anions, present in the buffer solutions used, possessed considerable influence on the Tafel-line slopes. The observed increase was attributed to the specific adsorption of such anions whence the evolution of hydrogen took place on a surface partly covered by these anions. In order to find out whether this is true of other metals or not, we have carried out a detailed study on the hydrogen overvoltage on molybdenum in pure hydrochloric acid and sodium hydroxide solutions or in a mixture of these and alkali phthalate, borate, phosphate or nitrate.

Experimental

The electrodes (Fig. 1) used in this investigation were spectroscopically pure rods, 5 mm. in diameter and 2 cm. in length, welded to glass tubings. Electric contact was maintained through a spiral copper wire fitted well around the tapering end of the rod lying inside the tube.

Fig. 1

The electrolytic cell was essentially similar to that of Bockris and Potter (*J. Chem. Phys.*, 1952, **20**, 614). It was constructed from pyrex glass and cleaned with chromic acid.

The electrolytes were pre-electrolysed (Azzam, Bockris, Conway and Rosenberg, *Trans. Faraday Soc.*, 1950, **46**, 918) for periods of 5 to 10 hours at a platinum gauze cathode, before immersion of the molybdenum electrode, while bubbling a stream of hydrogen, purified by the method of Honigschmidt (*Z. anorg. Chem.*, 1927, **163**, 78). The electrolysis was continued for another hour at the molybdenum cathode before the measurements were started. The Tafel lines were traced in unstirred solutions from a higher current density of 1.8×10^{-3} amps./cm^2. to a lower one of 1×10^{-5} amps./cm^2. The same results were obtained for both the periods.

Measurements were made in pure HCl solutions of concentrations varying from 5.9 to 0.003 *N* (p_H 1.05 to 2.55) and in 0.1 *N*-NaOH solution (p_H 13.0), either alone or when admixed from the start with phosphate, borate, nitrate or phthalate ions. HCl solutions were prepared from the constant boiling acid

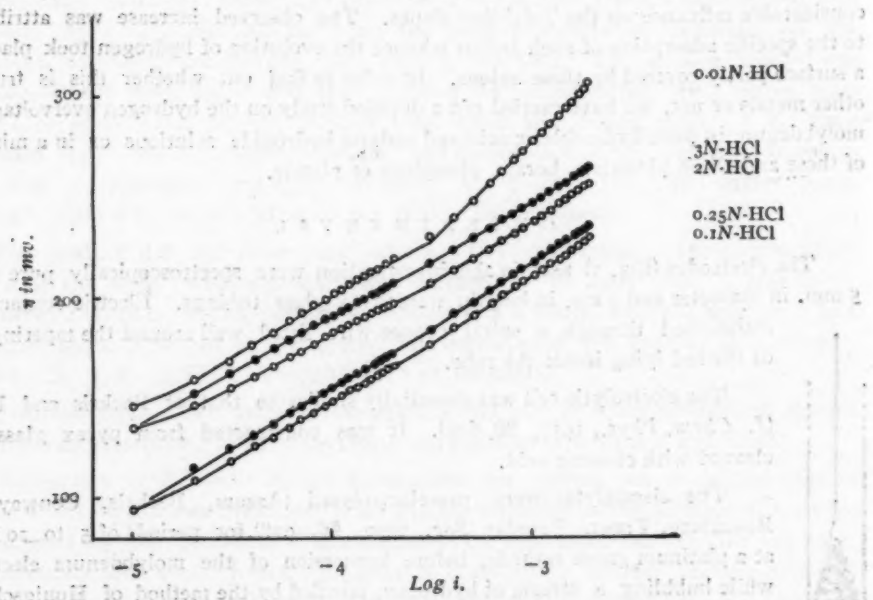
(5.91 *N*) by appropriate dilution with water (twice distilled from alkaline permanganate). The salts used were of the Analar samples. The calculated amounts were dissolved in acid or alkali hydroxide solutions to make them 0.05 or 0.1 molar with respect to the above anions. NaOH solutions were prepared by diluting the concentrated carbonate-free solution. The water used was twice distilled from alkaline permanganate.

The p_H of the solutions was measured at the end of each experiment using the hydrogen electrode.

Behaviour in Pure Hydrochloric Acid Solutions

Fig. 2 shows representative Tafel lines obtained in pure HCl solutions of ~ 5.9 to 0.003 *N*, using current densities ranging from 1×10^{-5} to 1.8×10^{-3} amps./cm² at 25°.

FIG. 2



The Tafel lines possess two slopes, one covering the current density range of 1×10^{-5} to 1.8×10^{-4} and the other within the range of 2×10^{-4} to 1.8×10^{-3} amps./cm². with the respective slopes 0.05 − 0.06 and 0.065 − 0.116v. In Table I are recorded the values of the slopes b_1 within the lower current-density range together with the respective i_{01} values, and the values of hydrogen overpotential η at the current densities 5×10^{-5}, 1×10^{-4} and 1.3×10^{-4} amps./cm². The values of b_2 and i_{02} within the higher current-density range together with η at the current densities 5×10^{-4}, 1×10^{-3} and 1.3×10^{-3} amps./cm². are listed in Table II.

TABLE I

Hydrogen overpotential at molybdenum cathodes in HCl *solns.*

Normality of HCl		5.90	5.0	4.0	3.0	2.0	0.50
p_H		−1.05	−0.930	−0.848	−0.598	−0.305	0.42
b_1		0.056	0.051	0.051	0.052	0.051	0.057
i_{01} amp./cm²×10⁻⁸		3	1.5	1.5	2.5	2.90	4.0
a		1.0	1.15	1.15	1.1	1.15	1.0
η in mv.	c.d. 5×10⁻⁵	174	182	185	175	165	151
	c.d 1×10⁻⁴	198	199	201	191	182	171
	c.d. 1.3×10⁻⁴	205	205	207	197	188	177
Normality of HCl		0.25	0.10	0.05	0.02	0.01	0.003
p_H		0.82	1.09	1.38	1.76	2.00	2.55
b_1		0.058	0.060	0.064	0.060	0.060	0.060
i_{01} amp./cm²×10⁻⁸		2.5	3.2	5.5	4.6	4.6	4.6
a		1.0	0.95	0.90	0.95	0.95	0.95
η in mv.	c.d. 5×10⁻⁵	136	129	134	182	182	178
	c.d. 1×10⁻⁴	155	147	152	200	202	200
	c.d. 1.3×10⁻⁴	162	155	159	207	209	207

TABLE II

Hydrogen overvoltage at molybdedum cathodes in HCl *solns.*

Normality of HCl		5.9	5.0	4.0	3.0	2.0	0.50
p_H		−1.05	−0.930	−0.848	−0.598	−0.305	0.42
b_1		0.066	0.064	0.065	0.060	0.066	0.072
i_{01} amp./cm²×10⁻⁸		10	7.8	1.5	10	2.2	2.2
a		0.85	0.90	0.90	0.95	0.85	0.80
η in mv	c.d. 5×10⁻⁴	238	236	238	228	217	212
	c.d. 1×10⁻⁴	257	255	257	247	237	235
	c.d. 1.3×10⁻⁴	265	263	264	255	245	244
Normality of HCl		0.25	0.10	0.05	0.02	0.01	0.003
p_H		0.82	1.09	1.38	1.67	2.00	2.55
b_2		0.073	0.076	0.090	0.095	0.100	0.116
i_{02} amp./cm²×10⁻⁷		1.7	2.2	6.3	2.5	1.6	2.5
a		0.8	0.75	0.65	0.60	0.60	0.50
η in mv	c.d. 5×10⁻⁴	196	191	197	244	248	254
	c.d. 1×10⁻⁴	218	211	220	267	277	287
	c.d. 1.3×10⁻⁴	227	218	228	275	290	302

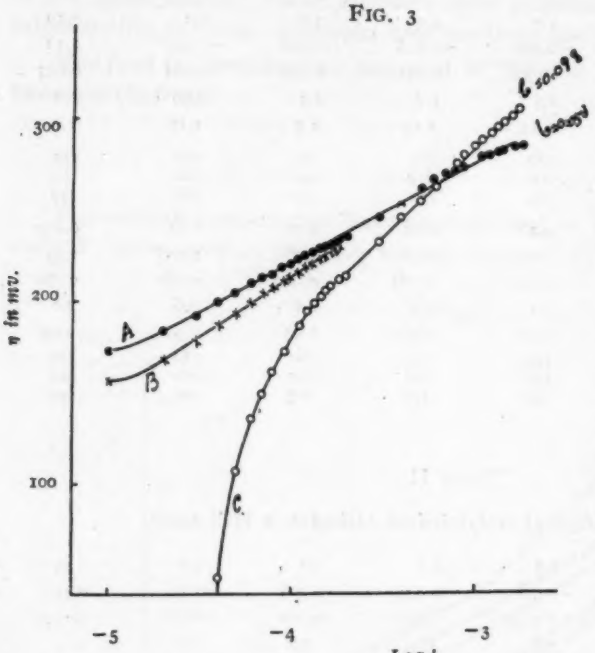
The above data show that η numerically decreases between $4N$ and $0.1N$-HCl with $d\eta/d\,p_H$ amounting to 29 mv. At lower acid concentrations ($0.1 - 0.003\ N$), η remains approximately constant at lower currents ($5 \times 10^{-5} - 1.8 \times 10^{-4}$) but increases numerically by $\sim$ 60 mv per unit p_H at higher currents ($5 \times 10^{-4} - 1.8 \times 10^{-3}$ amps./cm².). Above 4 N-HCl the values of η exhibit slight variations with p_H.

Effect of Anions on the Discharge of Hydrogen on Molybdenum

As was previously observed (Issa, Ammer and Khalifa, *loc. cit.*), anions possess a considerable effect on the slopes of the Tafel lines and on the values of η on chromium.

The same effect was observed in the case of molybdenum, as shown in Table III. The anions studied include phthalate, borate, phosphate and nitrate.

FIG. 3



A: p_H 0.085 HCl + phosphate.
B: „ 1.15 „ + phthalate.
C: „ 1.0 „ + nitrate.

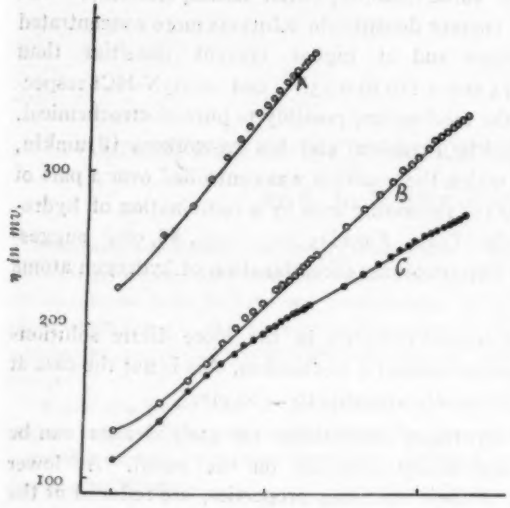
Nitrate anions produce a pronounced effect on the values of η and on the Tafel-line slope. Curve A in Fig. 3 shows that η in 0.1*N*-HCl + nitrate ($p_H^{\cdot} \sim 1.0$) and at low current densities is very small, amounting to 50 mv but rises rapidly such that the slope of the curve is 0.4 volt. On increasing i above 10^{-4} amps./cm^2., the curve becomes linear with a slope of 0.098, approximating thus the behaviour in pure acid solution, $b_2 = 0.073$. In alkaline solutions, the effect of the nitrate ion is much less pronounced and above 10^{-4} amps./cm^2., the behaviour is exactly similar to that in pure NaOH solution.

TABLE III

Solution.	p_H.	C.D. = 10^{-5} – 10^{-4} amp./cm^2. b_1.	i_0.	C.D. = 2×10^{-4} – 1.8×10^{-3} amp./cm^2. b_2.	i_0.
Pure HCl	1.0	0.058	3.0×10^{-5}	...	...
HCl + borate	1.12	0.060	3.2×10^{-5}	0.050	7.1×10^{-7}
„ + „	7.93	0 129	2.4×10^{-7}	0.246	6.3×10^{-6}
„ + „	8.12	0.132	2.2×10^{-7}	0.193	1.8×10^{-6}
Pure borate	8.71	0.131	2.3×10^{-7}	0.172	$1\ 5\times10^{-6}$
HCl + phthalate	1.15	0.054	2.0×10^{-5}	0.078	2.8×10^{-7}
„ + phosphate	0.085	0.053	2.0×10^{-5}	...	...
„ + nitrate	1.0	0.098	1.0×10^{-6}	...	...
Pure NaOH	13.0	0.072	3.2×10^{-5}	0.092	2.4×10^{-7}
NaOH + borate	12.14	0.082	$1\ 3\times10^{-7}$	...	...
„ + phthalate	11.90	0.075	3.2×10^{-5}	0.092	1.5×10^{-7}
„ + phosphate	12.00	0.100	$6\ 7\times10^{-7}$	...	...
„ + nitrate	13.00	0.075	6.3×10^{-5}	...	...

In acid solutions phosphate anions have no effect on the slope of the Tafel line (b amounting to ~0.053) or on the value of η (curve B, Fig 3). The slope of the Tafel line observed in pure NaOH solution of p_H 13.0 is higher than in pure HCl solutions, amounting to 0.072 and 0.092 within the lower and higher current-density range (curve A, Fig. 4). In presence of phosphate (p_H 12.0) and borate (p_H 12.14) the slopes are higher, amounting to 0.1 and 0.082 throughout the whole current-density range. A striking phenomenon, however, is that the borate anion has a pronounced effect on the Tafel-line slope obtained in solutions (HCl + borate) of p_H higher than 7. Thus, at p_H 7.93 and 8.12, slopes amounting to 0.129, 0.132 are obtained at lower currents and 0.246, 0.193 at higher ones respectively (see Table III). Similarly, the respective values obtained in 0.05 N pure borate solution of p_H 8.71 amount to 0.131 and 0.172, as compared to 0.06 and 0.09 in HCl + borate solution of p_H 1.12.

FIG. 4



A: p_H 12.14 NaOH + borate.
B: ,, 11.4 ,, + phthalate.
C: ,, 13.0 ,, + nitrate.

DISCUSSION

The values of parameters for the hydrogen evolution on molybdenum were calculated from the relations

$$\eta = RT/\alpha F \ln i_0/i_c \quad \text{or} \quad b = 2.303\, RT/\alpha F$$

in which i_0 is the exchange current and i_c, the current density corresponding to the overpotential η, and α is a constant. The parameters as found experimentally are listed in Tables I and II for the lower and higher currents respectively. The most probable value of α is "one" which is not in accordance with the observations previously made by Pecherskaya and Stender (*J. Appl. Chem. Russ.*, 1946, **19**, 1303) who obtained for α the value 0.5 in 2 N-H_2SO_4, and Bockris and Parsons (*Faraday Soc., Disc.*, 1947, **1**, 225, 95; *Trans. Faraday Soc*, 1948, **44**, 860) who obtained 0.5−1.5 in 1N-HCl.

The fact that the Tafel-line slope in concentrated and dilute acid solutions up to a current density of 1.8×10^{-4} amps./cm^2. amounts to ~ 60 mv indicates that the process of hydrogen evolution cannot be accounted for by any of the known simple mechanism. Thus, the slow discharge is characterised by a slope of 0.116 and a value of h (the electron number) = 1. The electrochemical mechanism has two slopes of 0.116 and 0 039 at high and low current densities respectively and a value of $h = 2$. The catalytic mech-

anism has at low current densities a slope of 0.03 and a value of $h = 2$. However, a dual mechanism, combining an electrochemical and catalytic processes, possesses a slope of 0.059 which lies near our experimental value (Ammar, Ph.D. Thesis, London). The mechanism remains the same at higher current densities in solutions more concentrated than 0.5 *N*-HCl. In more dilute solutions and at higher current densities than 1.8×10^{-4}, the slope increases up to 0.073 and 0.116 in 0.25*N*- and 0.003*N*-HCl respectively (Table II), indicating a change in the mechanism, possibly to pure electrochemical. Dual mechanisms were suggested for nickel by Frumkin and his co-workers (Frumkin, *Faraday Soc. Disc.*, 1947, **1**, 63) in which the reaction was controlled over a part of the electrode by a discharge step and over the remaining area by a combination of hydrogen atoms. Similarly Bockris and Conway (*Trans. Faraday Soc.*, 1949, **45**, 989) suggested a dual rate-determining desorption step involving recombination of hydrogen atoms and electrochemical desorption.

Although the effect of p_H on η at low current densities in the more dilute solutions is in agreement with the dual electrochemical-catalytic mechanism, this is not the case at higher currents when the average value of $d\eta/dp_H$ amounts to $\sim$ 60 mv.

The effect of the anions on the hydrogen overvoltage on molybdenum can be explained on the premise that they are specifically adsorbed on the metal. At lower currents the nitrate ions, on account of their oxidising properties, are reduced at the electrode surface. This behaviour resembles depolarisation of oxygen, when not rigidly removed from the solution prior to electrolysis. At higher currents, the process of adsorption decreases, but instead hydrogen deposition occurs and the Tafel line behaves normally. Phthalate anions, on the other hand, are without effect on the Tafel-line slope, obtained in an acid solution of p_H 1.15 and with but a slight effect in an alkaline solution of p_H 11.9, indicating a slight tendency of being adsorbed.

Borate ions, on the other hand, bring about a pronounced increase of both b and η values, especially at higher p_H, but the exact reason for this is not clear.

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ABSORPTION AND FLUORESCENCE SPECTRA OF FLAVONOLS

By S. K. K. Jatkar and B. N. Mattoo

Absorption and fluorescence spectra of a number of flavonols (with 4′-OCH_3 or 4′-$OCH_2\phi$ substitution) and flavonol-acetates have been reported and discussed. The additional absorption band in flavonol and its derivatives is due to keto-enol tautomerism. 4′-OCH_2.R (R = H, ϕ) group produces a bathochromic effect which is due to the increase in resonance by this substitution. Benzoyl group in 6-position modifies the spectrum radically, while conversion of 3-OH to 3-O.CO.CH_3 reverts the spectrum to that of flavone.

Fluorescence spectrum of flavonols has two bands in the visible. 4′-OCH_3 and 4′-$OCH_2\phi$ groups increase and benzoyl group greatly reduces the fluorescence efficiency. Acetylation of the hydroxyl at 3-position tends to revert the fluorescence spectrum to that of flavone, but there is a considerable decrease in efficiency.

Skarzynski (*Biochem. Z.*, 1939, **301**, 150) has shown that flavonol (3-hydroxyflavone) spectrum has an additional absorption band in the long-wave region, compared to other flavone spectra. This has been attributed to the possibility of tautomerism.

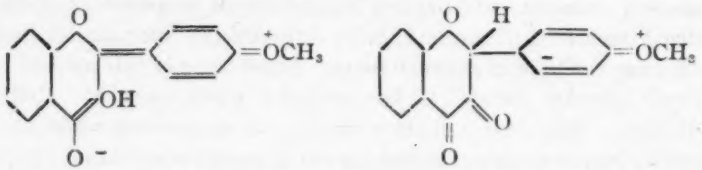
Study of fluorescence spectra of flavones or flavonols has not been reported so far. Qualitative study of the exhibition of fluorescence of flavones (including 3-hydroxy derivative) in relation to structural factors has been done by Seshadri and his co-workers (*Proc. Ind. Acad. Sci.*, 1940, **12A**, 375; 1951, **34A**, 319). Their work includes visual observation of the fluorescence, excited by daylight. Exciting radiation has not been considered in arriving at the conclusions.

The present work on absorption and fluorescence spectra of flavonols is discussed below. The data are shown graphically in Figs. 1-4.

Absorption

The flavonol spectra are a superposition of the spectra of two individual components present in different proportion, keto form being predominant. Flavonol shows another band in the 210 mμ region (not exactly located, as it was just beyond the range of the instrument under the experimental conditions) in addition to the three known bands at 240 (broad), 307 and 345 mμ. Due to the ionisation of the enol-tautomer, a regular change in absorption with p_H is observed. The absorption of the ionic form is higher in the region 400 mμ, while it is lower in the regions 340 and 300 mμ, as compared to that of the molecular form. The same is observed, though very prominently, with 7-hydroxycoumarins and chromones (work under publication). This p_H-dependence of absorption is shown in a similar manner by all other flavonols (not their acetates) studied here.

4′-OCH_3 substitution, which increases resonance,

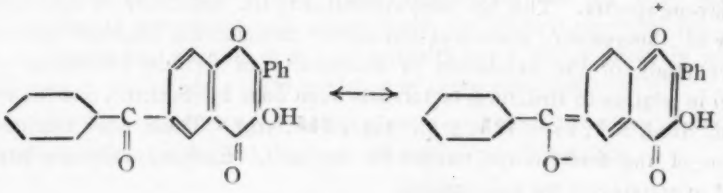


(Enolic). (Ketonic)

modifies the absorption spectrum in as much as the 345 mμ band of flavonol is shifted to 355.5mμ ; the 307 mμ band is shifted to 320 mμ but is now unresolved and appears as a very prominent shoulder. The higher-frequency bands at ~ 250 mμ (inflexion), 234 mμ, and ~ 220 mμ (inflexion) are observed instead of the single broad maximum of flavonol at 240 mμ. The appearance of the 320 mμ band as a prominent shoulder is common to all 4′-methoxy- or 4′-benzyloxyflavonols. The total absorption, $\int \epsilon dv$, of 4′-methoxyflavonol also increases to 76.7 (66.8 in case of flavonol).

The methyl substitutions at 6- and 7- positions in 4′-methoxyflavonol produce slight shift in absorption bands, and the bands in the high frequency region are now well resolved into three component maxima. The integrated absorption in neutral medium increases to 84.3 and 84.1 respectively.

The increase in resonance due to 6-benzoyl group produces a large bathochromic



effect ; now the longest-wave band is at 362.5 mμ and the nature of the spectrum in the shorter-wave length region is radically different. $\int \epsilon dv$ is very much increased and is now 112.2.

Replacement of 4′-OCH_3 by 4′-OCH_2? has a very similar effect as in flavones (Jatkar and Matto, this issue, p. 623).

Introduction of 6-methyl-3′-methoxy or 7 : 3′-dimethoxy groups in 4′-benzyloxyflavonol not only causes an appreciable increase in integrated absorption, but also modifies the shorter wave absorption further so that only a single band in this region, viz., 250 mμ and 247 mμ respectively, is exhibited now.

Acetylation of the hydroxyl of flavonols, as expected, reverts their spectra to those of the corresponding flavones. Now there being no possibility of keto-enol tautomerism, the spectrum is essentially similar to that of flavones, e. g. 6-methyl-4′-methoxyflavonol acetate has maxima at 321, 254 and 224.5 mμ, while 6-methyl-4′-methoxyflavone shows bands at 321.5, 254 and 223 mμ.

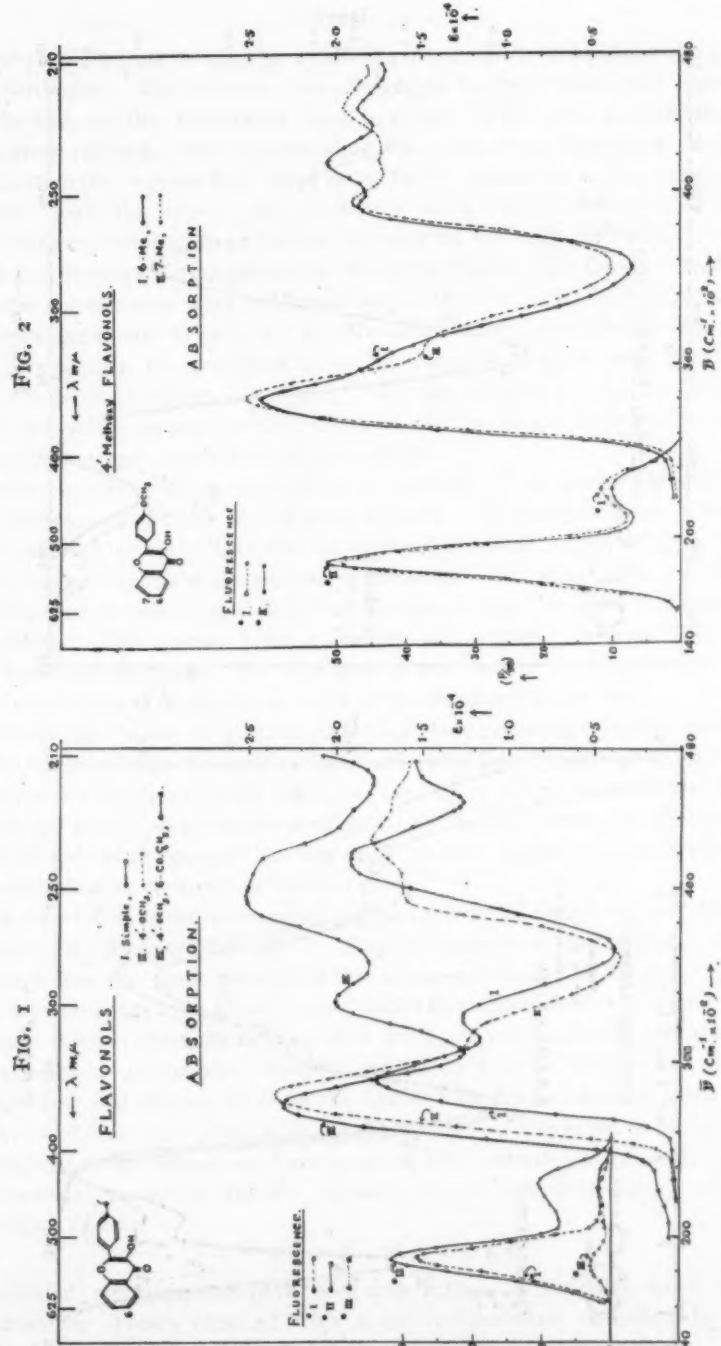


FIG. 1
FLAVONOLS
ABSORPTION.
I. Simple, ——
II. 4'-OCH3, ·····
III. 4'-OCH3, 6-CH2N, ——
FLUORESCENCE:
I ·····
II ——
III ——
λ mμ
ν̄ (Cm⁻¹ × 10³) →
FIG. 2
4'-Methoxy FLAVONOLS.
ABSORPTION
I. 6-Me, ——
II. 7-Me, ·····
FLUORESCENCE
I ·····
II ——
λ mμ
ν̄ (Cm⁻¹ × 10³) →

FIG. 3

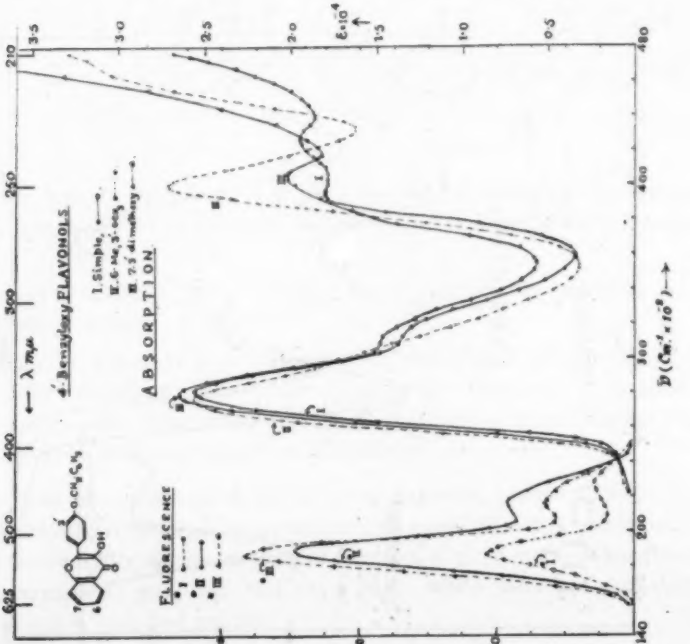
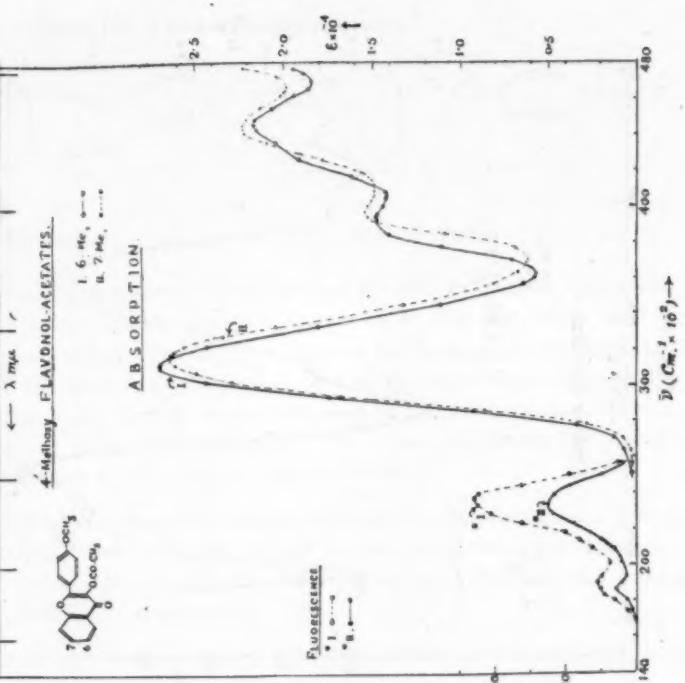

4'-Benzyloxy FLAVONOLS
I. Simple,
II. 6-Me, 3'-OCH3
III. 7,3'-dimethoxy
ABSORPTION
FLUORESCENCE
λ mμ
ν̄ (Cm.⁻¹ × 10³)

FIG. 4


4'-Methoxy FLAVONOL-ACETATES
I. 6-Me,
II. 7-Me,
ABSORPTION
FLUORESCENCE
λ mμ
ν̄ (Cm.⁻¹ × 10³)

Fluorscence

Flavonols differ from flavones in exhibiting an emission which has quite a different spectral distribution. The emission (visually green) has two bands, one comparatively weak in the blue and the other strong band in green. It is quite probable that the two bands are given rise to by the corresponding two long-wave absorption bands. This would mean that the weaker blue band is due to the absorption in the relatively weak "enol-band", while the stronger green emission band is due to absorption in the "keto-band". However, the frequency interval between the two emission bands is, in general, more than that between the corresponding absorption bands of the flavonols studied here.

Flavonol shows a very weak and broad band in the blue (~440 mμ), while a comparatively strong maximum at 535 mμ. 4′-OMe substitution increases the emission, the relative $\int Fdv$ being 1, 130 compared to 740 for flavonol, though there is also a corresponding increase in $\int \epsilon dv$ from 66.8 to 76.7. The blue band at 435 mμ for the former is comparatively much strong; relative F_{max} at this wave-length being 208 and 32 for 4′-methoxyflavonol and simple flavonol respectively.

Introduction of methyl group at 6- or 7- position of 4′-methoxyflavonol increases the total fluorescence and also the efficiency slightly. There is no change in the position of the fluorescence bands. With the replacement of 4′-OCH_3 by 4′-$OCH_2\varphi$ there is no significant change except a slight increase in efficiency. But when 6-Me- 3′-OMe or 7-3′-diOMe groups are introduced in 4′-benzyloxyflavonol, a large increase in efficiency (about 2 times) results. This increase is much less than that found in flavones (7-8 times) as a result of these substitutions. The blue band of the emission is shifted to 465 mμ (from 440 mμ), while there is no significant shift in the maximum at 540 mμ.

6-Benzoyl derivative of 4′-methoxyflavonol behaves similar to the corresponding flavone in having a large decrease in efficiency ($\int \epsilon dv$ and relative $\int Fdv$ for 6-benzoyl-4′-methoxy and 4′-methoxy being 112.2, 130 and 76.7, 1, 130 respectively) and also a red-shift in the green maximum ($\Delta\lambda = 10$ mμ). The large decrease in efficiency may be due to hindrance of the normal electron drift towards pyrone oxygen at 4-position, by the introduction of an electrophilic benzoyl group.

With acetylation of the hydroxyl of the flavonols, their behaviour reverts to that of the corresponding flavones (*vide supra*). Now the emission is mainly blue. The flourescence band has the same position as that of the corresponding flavone (λ^F_{max}, 6-Me, 4′-OCH_3-flavone = 425 mμ ; λ^F_{max}, 6-Me-4′-OCH_3-flavonol-acetate = 425 mμ). However, a very slight flavonol character remains in as much as a comparatively very week band at 530 mμ persists. Acetylation, besides, results in a large decrease in fluorescence efficiencey : $\int \epsilon dv$ and relative $\int Fdv$ for the flavone and flavonol-acetate, cited above, are 85.7, 1170 and 82.0, 425 respectively. Had the link —O— behaved as perfect insulator, then -O-CO-CH_3 group should not have hindered any normal electron drift towards the pyrone oxygen at 4-position, and the efficiency would have been similar to that of the corresponding flavone.

Experimental

Absorption measurements have been done with a Beckman DU spectrophotometer and fluorescence spectra obtained with a spectrofluorimeter described by Jatkar and Mattoo (*J. Univ. Poona*, 1954, No. **6**, 67).

Absorption spectra were measured in aqueous alcohol (87%) in neutral, $10^{-4}N$-HCl and $10^{-4}N$-KOH solutions, while the fluorescence was studied of alcoholic (96%) solutions. Concentrations were throughout kept at $0{\cdot}5 \times 10^{-4}$ *M*. The accuracy in the measurement of ϵ is within 1% and $\bar{\nu}_{max}$ are correct to $\pm$ 0.2%. For measuring the integrated absorption (limits 2, 100 Å and 5, 000 Å) and fluorescence, the areas under the respective spectral curves (on $\bar{\nu}$ scale) were measured planimetrically. In a qualitative comparison of fluorescence efficiencies of these compounds, the spectral distribution in the exciting radiation has not been taken into account.

The compounds used were pure as judged by their m.p.'s.

Thanks are due to Dr. M. G. Marathey for making the compounds available for the present study.

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ABSORPTION AND FLUORESCENCE SPECTRA OF BENZYLIDENE-COUMARANONES

By S. K. K. Jatkar and B. N. Mattoo

Absorption and fluorescence spectra of 4′-methoxy- and 4′-benzyloxy-benzylidene coumaranones have been reported and discussed. Effect of various substitutions has been studied.

Though strong fluorescence is met with in the solid state, the efficiency is low in solution. There is an appreciable 'inner-filter' effect.

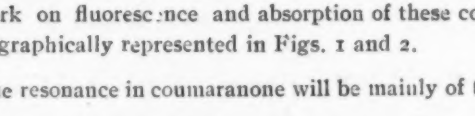
Absorption spectrum of coumaran, reported by Jones and Lindsay (*J. Chem. Soc.*, 1950, 1836), shows one band beyond 2,000Å, having fine structure (282, 289mμ). Some coumaranone or coumaran-3-one derivatives have been studied by Smith and Boyack (*J. Amer. Chem. Soc.*, 1948, **70**, 2687). The spectrum of 2-*iso*propyl-4 : 6 : 7-trimethyl derivative, for instance, shows two bands beyond 2,000Å, viz., 287 mμ and 260 mμ.

Substitution of a $=CH—C_6H_5$ group in 2-position in coumaranone, which is in conjugation with C=O, changes the spectrum altogether, as expected. Now the benzylidene-coumaranone (e.g. 6 : 7-dimethoxy-3′-amino) shows two bands at 252 mμ and 310 mμ (cf. Price *et al.*, *ibid.*, 1934, **56**, 2483). The $-NH_2$ group in 3′-position, as in the above example, cannot produce such additional resonance, as when in 4′-position. Thus, the isomeric compound, 6 : 7-dimethoxy-4′-amino derivative shows bands at 257 mμ and 445 mμ. There is, however, a broad shoulder on the short-wave side of the 445 mμ band. The absorption has now shifted right into the blue end of the visible, because of high electron-donating capacity of $-NH_2$. As the resonance theory of colour (Bury, *ibid.*, 1935, **57**, 2115) was not proposed when Price *et al.* studied the absorption spectra of the *p*- and *m*- aminobenzylidene-coumaranones, their doubts about such a large difference in absorption spectrum by changing $-NH_2$ from 3′- to 4′- position were not unjustified.

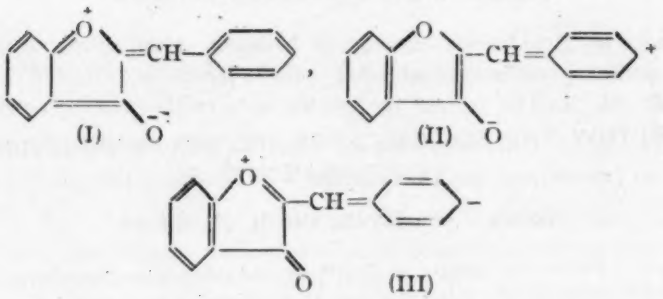
No work on the fluorescence of benzylidene-coumaranones is reported so far.

The present work on fluorescence and absorption of these compounds is discussed below ; the data are graphically represented in Figs. 1 and 2.

Absorption.—The resonance in coumaranone will be mainly of the type :



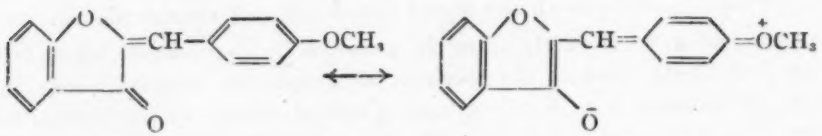
Substitution of benzylidene group in 2-position will increase the resonance and the following dipolar structures will contribute appreciably to the excited state resonance hybrid :



(I) (II) (III)

Resonance of the type (III) will be inhibited by electron-donating groups present in 4′-position. As the present study includes benzylidene-coumaranones with *para* ↶ OR substitution, we may not consider the resonance of the type (III).

In *p*-methoxybenzylidene-coumaranone or 4′-methoxybenzylidene-comaranone, the resonance of the type (II) will be appreciably increased.



Thus, we find its absorption spectrum extending right into the visible, with strongest maximum at 402 mμ ($\epsilon = 28,500$). The other maxima include those at 540 (very broad and weak), 342, 256 and 225 mμ with $\epsilon = 780$, 14760 15540 and 9040 respectively. The integrated absorption $\int \epsilon d\nu$ (76.0) is not very much different from that of the corresponding isomeric (4′-OCH_3) flavone (74.5).

Introduction of 5-Me or 7-Me groups was found to produce a slight bathochromic shift in longest-wave absorption band ($\Delta\lambda = 5$ mμ and 3 mμ respectively). Slightly lower values of $\int \epsilon d\nu$ of the Me- substituted derivatives, and appreciably lower ϵ_{max} values in the 4,000Å band first gave rise to doubts about the purity of the 4′-methoxy derivative, but the values were confirmed after repeating the measurements with a repurified sample. The unusual behaviour of alkyl groups in this case is not clear at present.

Substitution of 6-Me, 3′-OCH_3, 4′-benzyloxy groups in benzylidene-coumaranone changes the nature of the spectrum in the high-frequency region ; absorption in the longest-wave band being little affected. Thus, it shows absorption bands at 405, ~330, 275 and 255 mμ.

Fluorescence.—Though benzylidene-coumaranones were found to emit brilliant green fluorescence in solid state, when examined under a Wood's lamp, these in solution emit only feeble blue fluorescence. Qualitative comparison of relative efficiencies with the isomeric flavones is not possible with the data collected, as the absorption spectra are radically different and taking the spectral distribution in the exciting radiation into consideration is very essential.

FIG. 1

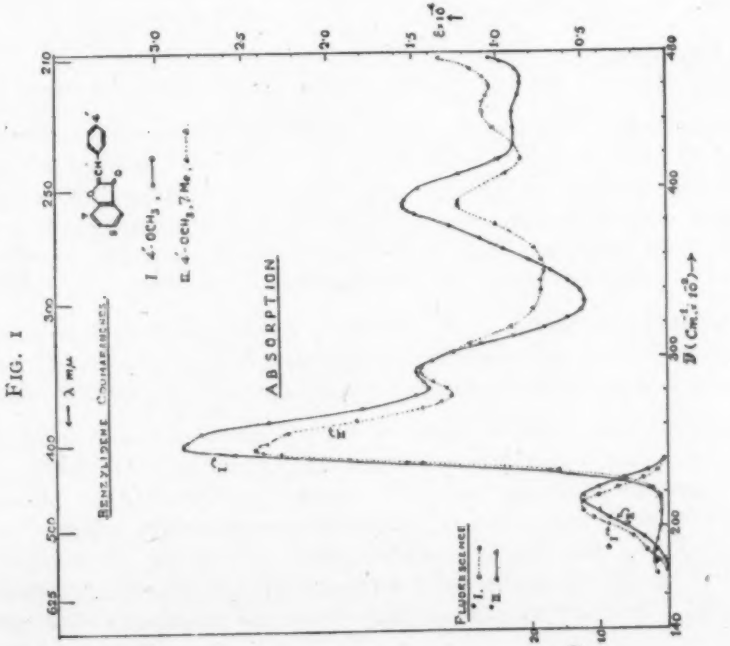
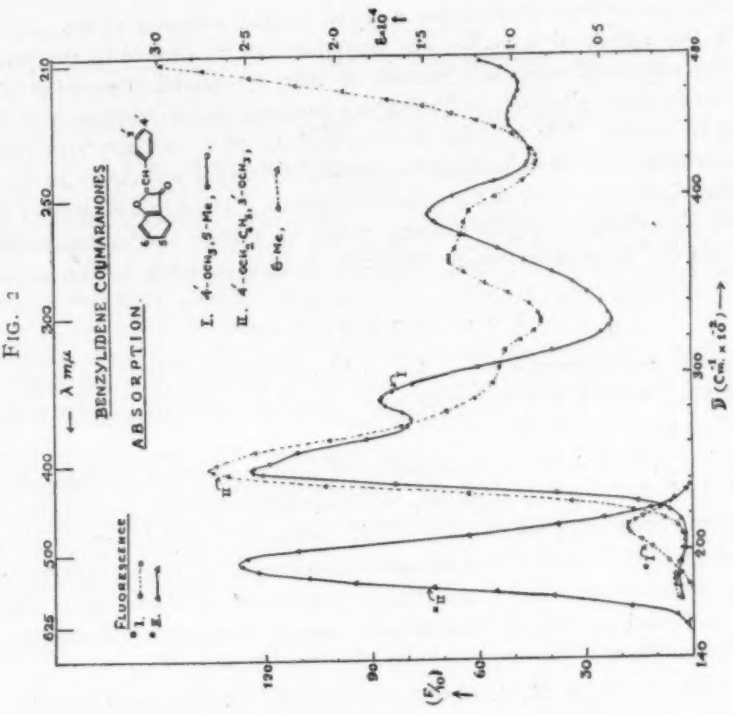

BENZYLIDENE COUMARANONES
ABSORPTION
FLUORESCENCE
I. 4'-OCH3
II. 4'-OCH3, 7-Me
λ mμ
ν̄ (Cm.-1 × 10³)
ε·10⁻⁴
(F/F0)

FIG. 2


BENZYLIDENE COUMARANONES
ABSORPTION
FLUORESCENCE
I. 4'-OCH3, 5-Me
II. 4'-OCH2C6H5, 3'-OCH3, 6-Me
λ mμ
ν̄ (Cm.-1 × 10³)
ε·10⁻⁴
(F/F0)

4′-Methoxybenzylidene-coumaranones have a blue emission (4,200-5,600Å) with maxima in the region of 4,700Å. The emission will be affected by the 'inner-filter' effect of the unexcited molecules because of their appreciable absorption in the blue region. The 6-methyl-3′-methoxy-4′-benzyloxy analogue has a much greater efficiency ($\int \varepsilon d\nu = 89.0$, relative $\int F d\nu = 2{,}130$ as compared to 76.0 and 200 respectively for 4′-OCH_3 analogue, and its λ^{F}_{max} is also red-shifted to 515 mμ ($\Delta\lambda = 40$ mμ), shown also by the change in colour of the emission to green. The effect of such substitutions as 6-methyl, 3′-methoxy or 7 : 3′-dimethoxy group in 4′-benzyloxybenzylidene-coumaranones in causing large increase in efficiency, is also common to the corresponding flavones.

EXPERIMENTAL

Absorption measurements were done with a Beckman DU spectrophotometer and fluorescence spectra obtained with a spectrofluorimeter (cf. Jatkar and Mattoo, *J. Univ.Poona*, 1954, No. 6, 67).

Absorption spectra have been measured in aqueous alcohol (87%), in neutral, $10^{-4}N$-HCl and $10^{-4}N$-KOH solutions, while fluorescence was studied in alcoholic (96%) solution ; concentration = $0.5 \times 10^{-4}M$. Integrated absorption (2,100-5,000Å) and fluorescence were computed from the areas of the respective spectral curves ($\bar{\nu}$ -scale), measured planimetrically. For a qualitative comparison of fluorescence efficiencies, the spectral distribution of the exciting radiation has not been taken into account.

The compounds used were pure as judged by their m.p.'s.

Thanks are due to Dr. M. G. Marathey for making the compounds available for the present study.

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ABSORPTION SPECTRA OF DIHYDROFLAVONOLS

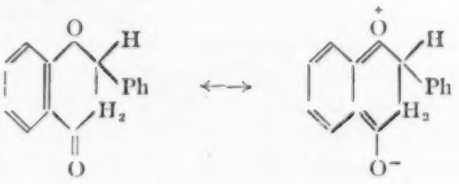
By S. K. K. Jatkar and B. N. Mattoo

Absorption spectra of 4′-OCH_3- 6-Me-4′-OCH_3- and 7-Me 3′-OCH_3- 4′-$OCH_3\phi$- dihydroflavonols are reported and discussed. The spectra are very similar to that of flavanone. 4′-OCH_3 or 4′-$OCH_3\phi$ substitution does not alter the nature of the spectrum, because these are not in conjugation with C=O and no additional resonance is possible. Reduction of pyrone double bond inhibits the fluorescence.

No work on absorption or fluorescence spectra of dihydroflavonols is reported so far. However, the absorption spectra of flavanones are reported, flavanone being the basic unit in dihydroflavonol (cf. Aronoff, *J. Org. Chem.*, 1940, **5**, 561).

Flavanones are reported to be non-flourescent, when examined in H_2SO_4 solution and excited by daylight (Sreerama Murti *et al.*, *Proc. Ind. Acad. Sci.*, 1951, **34A**, 319).

The present work was undertaken with a view to ascertaining the effect of the reduction of pyrone double bond in flavones. The resonance in flavanone should be essentially similar to chromone :

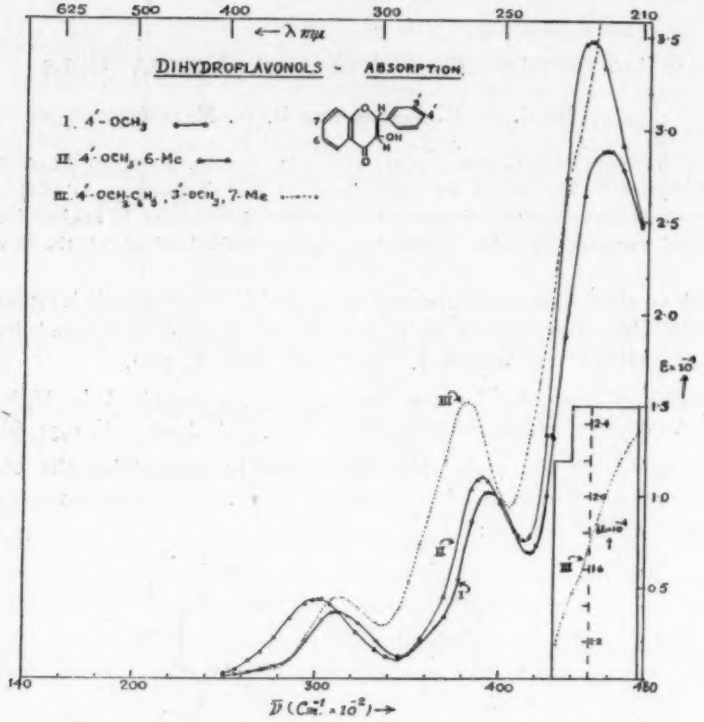


In accordance with the fact that the phenyl group, even now, cannot resonate with the rest of the molecule, the spectra of dihydroflavonol and its 4′-OCH_3 derivatives are found to be similar to the flavanone spectrum (see Fig. 1). However, the reduction of the pyrone double bond affects the transition probability to a large extent, which is shown by its much smaller integrated absorption ($\int \epsilon dv$ for 4′-methoxydihydroflavonol and 4′-methoxyflavone being 47.0 and 74 5 respectively).

Introduction of methyl group at 6- position of 4′-methoxydihydroflavonol shifts the bands to red. The bands at 332, 256 and 224 mμ have oscillator strengths of 0 09, 0.17 and 0.60 respectively. The total integrated absorption increases from 47.0 to 56.5.

Inhibition of fluorescence occurs by the reduction of the pyrone double bond due to significant decrease in resonance. The dihydroflavonols were found to be practically non-fluorescent when excited by hydrogen discharge—6-methyl-4′-methoxy derivative, however, exhibited a very feeble green emission. The same compounds, when examined under comparatively strong Hg emission lines 4,047Å and 3,660Å, exhibited a just perceptible green emission. The resonance being more or less similar to chromones without any hydroxyl, which are non-fluorescent, the same behaviour is to be expected of dihydroflavonols.

Fig. 1



EXPERIMENTAL

Absorption measurements were done with a Beckman DU spectrophotometer. Absorption has been measured in neutral, $10^{-4}N$-HCl, and $10^{-4}N$-KOH media; solvent 87% alcohol ; concentration, $0.5 \times 10^{-4}M$. For measuring $\int \varepsilon d\nu$ (limits 2,100-5,000Å) the area under the absorption curve ($\bar{\nu}$ scale) was measured planimetrically.

The compounds used were pure as judged by their m.p.'s.

Thanks are due to Dr. M. G. Marathey for making the compounds available for the persent study.

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ALTERNATING CURRENT ELECTROLYSIS. PART V. FORMATION OF CHLORATE AND HYPOCHLORITE DURING A.C. ELECTROLYSIS OF HOT SODIUM CHLORIDE SOLUTIONS

By K. M. Joshi

Electrolysis of saturated solution of sodium chloride at 70°, using platinum electrodes with symmetrical alternating current, has been carried out under various conditions of frequency, current density and p_H, using $K_2Cr_2O_7$ as a depolariser.

It is observed that increasing the frequency of alternation, the current efficiency of chlorate as well as hypochlorite formation decreases, so much so that at high frequencies no hypochlorite is detected. With higher current densities, the current efficiency of chlorate as well as hypochlorite formation increases as against the fact that in D.C. electrolysis, the current efficiency of hypochlorite formation decreases with current density. Addition of HCl to the electrolyte has been found to decrease the current efficiency of chlorate formation while in D.C. electrolysis, it increases with the addition of HCl. Hypochlorite efficiency also decreases with the addition of HCl in A.C. as well as in D.C. electrolysis.

Explanation of the observed phenomena, based on recombination reactions taking place at the electrodes, has been offered.

This investigation is in continuation of our previous work on A.C. electrolysis (this *Journal*, 1952, **29**, 69; 1954, **3**, 275)

The production of chlorate and hypochlorite in D.C. electrolysis has been investigated in detail by several workers (Foerster and Dolch, *Z. Elektrochem.*, 1917, **23**, 137; Foerster and Jorre, *J. prakt. Chem.*, 1899, **59**, 53; Müller, *Z. Elektrochem.*, 1899, **5**, 469) and the process is worked on a commercial basis also. It has been shown that in neutral and alkaline solutions, chlorate formation takes place by electrochemical oxidation of ClO^-, discharged at the anode, the ClO^- being produced by the combination of Cl_2 and NaOH, formed at the anode and cathode respectively:

$$Cl_2 + 2\ NaOH \longrightarrow NaClO + NaCl + H_2O \quad \ldots (1)$$

$$6\ ClO^- + 3\ H_2O \longrightarrow 2\ ClO_3^- + 4\ Cl^- + 6\ H^+ + 1\tfrac{1}{2}\ O_2 + 6e \quad \ldots (2)$$

In acid solutions, however, the current efficiency is much greater as the production of chlorate can take place in the entire electrolyte according to

$$2\ HClO + ClO^- \longrightarrow ClO_3^- + 2\ Cl^- + 2\ H^+ \quad \ldots (3)$$

It was therefore thought that by using NaCl as the electrolyte in A.C. electroysis, current efficiency of chlorate formation would give an idea of different combination and discharge reactions taking place at or near the electrode.

Experimental

The experimental arrangement was the same as that used in previous investigations (*loc. cit.*).

The electrolyte contained 300 g. of NaCl and 3 g. of $K_2Cr_2O_7$ per litre. NaCl used was Merck's reagent quality, purified by recrystallisation. Polished platinum electrodes, measuring 2 × 2 cms., were used.

The electrolyte (500 c.c.) was taken for each run of electrolysis. The temperature of the electrolyte was maintained at $70° \pm 2°$. For comparison, an exactly similar cell was placed in the D.C. portion of the circuit. For each experiment, the electrodes were cleaned with HNO_3 (hot, conc.), washed with water and heated to redness before use.

Hypochlorite was estimated against standard sodium arsenite, using starch and KI as external indicator. Chlorate was estimated by adding an excess of KI to the solution and heating in sealed bottles (Vogel, "Quantitative Analysis", p. 423). Iodine liberated was titrated against standard thiosulphate. By subtracting equivalent hypochlorite titre, the amount of chlorate could be evaluated. Distance between the electrodes was always 7 cms. The electrolyte was not stirred.

TABLE I

Effect of frequency on the current efficiency of chlorate and hypochlorite formation.

Platinum electrodes: 8 sq. cm. Current = 1 amp. Amp. hrs. passed = 4.

Frequency per sec.	% C.E of ClO_3^- formation.		% C.E of ClO^- formation.	
	D.C.	A.C.	D.C.	A.C.
5	47.96	12.81	36.70	9.95
10	58.30	6.32	37.54	8.10
20	59.40	5.98	37.00	6.18
30	54.70	3.10	27.00	1.50
40	55.05	1.05	24.70	Nil
50	54.80	0.60	21.10	Nil

C.E. denotes current efficiency.

From Table I the current efficiency of chlorate formation in A.C. electrolysis appears to fall with the frequeney of alternation, and at higher frequencies it nearly falls to zero. This is also the case with the hypochlorite formation during A.C. electrolysis. At high frequencies, amount of hypochlorite formed in solution is zero. The efficiency in A.C. electrolysis even at as low a frequency as 5 per second is only about $\frac{1}{4}$th the current efficiency in direct current electrolysis.

TABLE II

Effect of current density on the current efficiency of chlorate and hypochlorite formation.

Platinum electrodes: 8 sq. cm. Ampere hours passed = 4.

C.D. (ma/sq.cm.)	% C.E. of ClO_3^-.		% C.E. of ClO^-.		C.D. (ma/sq.cm.)	C.E. of ClO_3^-.		C.E. of ClO^-.	
	D.C.	A.C.	D.C.	A.C.		D.C.	A.C.	D.C.	A.C.
	Frequency = 10 per second.					Frequency = 40 per second.			
250	58.30	6.32	37.54	8.1	250	55.05	1.05	24.70	0.0
500	70.50	22.18	27.14	11.1	500	62.16	8.46	24.06	1.6
750	71.03	29.44	23.15	10.05	750	88.80	30.80	4.60	1.6
					1000	84.10	38.30	1.00	17.6

C.D. denotes current density.

In A.C. electrolysis, the C.D. plays an important part. The C.E. of chlorate as well as hypochlorite formation increases with C.D. It is significant that the efficiency of hypochlorite formation decreases with C.D. in D.C. electrolysis as against the observed increase during A.C. electrolysis. Another point that is of importance is that by using fairly high current densities, chlorate yield in A.C. electrolysis can be as high as 38% or more.

TABLE III

Effect of addition of 1.58 *N*-HCl *to the electrolyte.*
Frequency = 10 per sec. C.D. = 500 ma/sq. cm.
Ampere hours passed = 4. Electrodes : platinum.

HCl added to 500 c c. of electrolyte.	% C.E. of ClO_3^-.		% C.E of ClO^-.	
	D.C.	A.C.	D.C.	A.C.
0 c.c	70.5	27.15	22.18	11.10
5	71.3	23.20	10.40	11.00
10	72.3	80.18	8.10	10.60
20	75.8	15.29	7.45	10.20
25	78.6	12.18	6.73	9.02
30	80.6	10.21	6.32	8.84
40	82 34	8.11	5.86	8.00

Thus, addition of HCl diminishes the yield of chlorate in A.C electrolysis as against the increased production of chlorate in D.C. electrolysis. The hypochlorite formation shows a rapid decrease with the addition of HCl in D.C. electrolysis ; with A.C., however, hypochlorite formation is not appreciably affected.

DISCUSSION

During A.C. electrolysis of NaCl solution, hydrogen and alkali are formed during the cathodic half-cycle and chlorine is evolved during anodic half-cycle. If we assume that the evolution of hydrogen can take place only after the complete saturation of the electrode surface with molecular hydrogen, it is likely that a portion of the hydrogen, discharged during the previous half-cycle, may still be on the electrode surface when chlorine discharge takes place. Hence, recombination reactions that can take place may be :

$$H\ldots(\text{Metal}) + Cl^- \longrightarrow H^+ + Cl^- + e \quad \ldots (4)$$

$$Cl^- + Cl^- \longrightarrow Cl_2 + 2e \quad \ldots (5)$$

$$Cl_2 + OH^- \longrightarrow Cl^- + Cl.OH \quad \ldots (6)$$

$$H^+ + OH^- \longrightarrow H_2O \quad \ldots (7)$$

As the frequency is increased, the duration of each half-cycle becomes smaller, and hence, the primary discharge products, discharged on the electrode, have very little time either to evolve as gas or combine or diffuse into the bulk of the solution, with the result that recombination of discharged products at the electrodes becomes more predominant than the other electrode reactions, leading to the formation of chlorate

or hypochlorite. Thus, we find at a frequency of 50 cycles, there is no hypochlorite in solution, while the chlorate efficiency is as low as 0.6%.

The increase in current efficiency of chlorate formation with increase in C.D. as also the slight increase of C.E. of hypochlorite formation with C.D. in A.C. electrolysis are understandable on the basis of the theory proposed (*vide supra*). At higher C.D. in a given interval of time, the amount of the discharged product round and near the electrode is much larger so that a high concentration of these discharged products exists on and in the vicinity of the electrode surface. As a result of this, the velocity of diffusion of these products into the bulk of the solution is greater. It is not to be understood that the diffusion of products will predominate over recombination reactions. The amount diffusing would always be small since the duration of one half-cycle is of the order of 1/10 sec. or smaller. The recombination reactions predominate in those cases where high current densities are employed, but the gradual increase in the hypochlorite concentration in the bulk of the solution as a result of diffusion may bring about the formation of chlorate (as in D.C. electrolysis) according to reaction (3).

The addition of H^+ ions to the electrolyte is shown to have quite the reverse effect with respect to chlorate formation as against the observed increase in C.E. in D.C. electrolysis. In the latter case, chlorate is produced by the oxidation of ClO^- by free HClO, which in turn is produced by H^+ from added mineral acid and ClO^-, formed at the electrode. This reaction in D.C. electrolysis is known to take place in the bulk of the electrolyte as H^+ ions are liberated as a result of this reaction. In A.C. electrolysis, the addition of H^+ to the solution removes the ClO^- as undissociated HClO so that the concentration of ClO^- in the vicinity of the electrode decreases resulting in the depletion of ClO^- at the electrode, and the discharge of Cl^- during anodic cycle predominates over the ClO^- discharge. Thus, the oxidation of ClO^- according to reaction (2) diminishes with the addition of a strong acid like HCl. Any small ClO^- concentration in the solution will combine with HClO, resulting in the formation of chlorate during reaction (3). Thus, the ClO^- efficiency diminishes as increasing amount of acid is added in A.C. electrolysis.

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A STUDY OF THE NATURE OF THE AQUEOUS LAYER AFTER EXTRACTION OF THE ETHERIAL BLUE PEROXYCHROMIC ACID

By Ramchandra Rai

Blue peroxychromic acid was prepared by taking constant volumes of 4% chromic acid solution and ether, and varying amounts of 20 vol. hydrogen peroxide were added. The ethereal peroxychromic acid was separated by means of a separating funnel. The aqueous layer was investigated by taking 10 c.c. of the solution in a weighed silica crucible, evaporating on a water-bath and igniting. Another 10 c.c. of the solution was iodimetrically titrated against a standard hypo solution. From 10 c.c. of the solution chromium hydroxide was precipitated by means of a dilute NaOH solution, washed and ignited. From the results the aqueous layer has been found to be chromium chromate which appears to be suspended in solution from which it is precipitated after a week or so.

During the study of the constitution and the chemical properties of the blue peroxychromic acid Berthelot (*Compt. rend.*, 1889, **108**, 477) observed the formation of a brown substance with weaker acids and potassium dichromate and hydrogen peroxide. The phenomenon was found to be more pronounced when hydrogen peroxide was added to an aqueous solution of potassium dichromate. A brown substance was found to be formed with effervescence, and after sometime the brown substance was decomposed and the liquid again attained the colour of the solution of potassium dichromate. The solution neither contained reduced chromic oxide nor hydrogen peroxide. The brown compound was considered to be probably a loose compound of hydrogen peroxide with chromic oxide. It decomposes rapidly with generation of chromic acid, liberation of oxygen and formation of water. The brown colour of the unstable intermediate product points to the formation of chromium chromate. The hydrogen peroxide oxidises the chromium chromate, forming chromic acid and water.

Bobtelsky, Glasner and Bobtelsky (*J. Amer. Chem. Soc.*, 1945, **67**, 966) during the study of catalytic decomposition of hydrogen peroxide with chromic acid by the method of absorption of light, are of the view that during the above reaction two compounds are formed- one, the blue and the other, violet or brown. They did not make any attempt to study the nature of the two compounds, simultaneously formed during the reaction of chromic acid and hydrogen peroxide. It is a well-known fact that the blue substance can be extracted with ether, and it is known as blue peroxychromic acid. Since no attempt is reported to have been made to study the nature of the aqueous layer, an investigation has been made to ascertain the nature of the aqueous layer after the separation of the blue peroxychromic acid by means of ether.

Experimental

When hydrogen peroxide is added to a chromic acid solution and ether, the blue peroxychromic acid formed goes into the ethereal layer which is separated by means of a separating funnel. The aqueous layer, which is left over, does not possess

the coloration of the chromic acid, but attains a brown colour. When to a portion of this brown solution a sodium hydroxide solution is added, a green precipitate of chromium hydroxiede is formed, which indicates that chromium is present in the basic part of the compound in the aqueous layer. If to the other portion of the above solution acetic acid and lead acetate solutions are added, a yellow precipitate of lead chromate is formed which indicates that chromate is also present in the above solution. In order to investigate the nature of the aqueous layer, the solution was obtained by keeping 100 c.c. of a 4% chromic acid solution in a Jena bottle in ice till the temperature of the solution attained that of ice. To this solution 100 c.c. of ice-cooled ether was added and to this mixture ice cooled solution of 2.5*N* hydrogen peroxide was added in varying amounts (10 to 200 c.c.), keeping the volumes of chromic acid solution and ether constant. The blue peroxychromic acid formed was separated by means of a separating funnel and the aqueous layer was taken in a separate Jena bottle and was left for about 24 hours in order that any unchanged hydrogen peroxide might be decomposed. The decomposition of hydrogen peroxide was ensured by the fact that on acidification of the solution, no blue peroxychromic acid was formed.

From the aqueous layer a 10 c.c. portion was taken in a weighed silica crucible, evaporated on a water-bath, ignited to convert it into Cr_2O_3, cooled in a desiccator and weighed. Another 10 c.c. portion of the same solution was titrated iodimetrically against a standard thiosulphate solution. A third 10 c.c. portion from the same solution was taken in a beaker and precipitated as chromium hydroxide by means of a dilute sodium hydroxide solution, filtered through a gravimetric filter paper, washed free of NaOH and chromate ions, dried and ignited in a weighed silica crucible, and the weight determined. Thus, the weight of Cr_2O_3 corresponding to the amount of chromium in the basic portion of the compound was found. From the volumetric results the amount of substance present as chromate in 10 c.c. of the solution was calculated. The results are tabulated below.

TABLE I

From 10 c.c. of the aqueous layer.

H_2O_2 added.	$Cr_2(CrO_4)_3$.	Cr_2O_3.	Ratio $\frac{Cr_2(CrO_4)_3}{Cr_2O_3}$	H_2O_2 added.	$Cr_2(CrO_4)_3$. layer.	Cr_2O_3.	Ratio $\frac{Cr_2(CrO_4)_3}{Cr_2O_3}$
10 c.c.	0.3731 g.	0.2212 g.	1.60	90 c.c.	0.1791 g.	0.1520 g.	1.17
20	0.2711	0.2272	1.19	100	0.1636	0.1382	1.18
30	0.2274	0.1878	1.20	110	0.1575	0.1346	1.17
40	0.1917	0.1624	1.17	120	0.1321	0.1196	1.10
50	0.1428	0.1246	1.15	140	0.1044	0.0994	1.05
60	0.1666	0.1428	1.15	160	0.1107	0.0982	1.05
65	0.1422	0.1262	1.13	180	0.0930	0.0882	1.06
80	0.1404	0.1248	1.12	200	0.0992	0.0984	1.05

When the amount of chromium oxide obtained from two molecules of chromium chromate is calculated, it is found to be as follows:

$$2\ Cr_2(CrO_4)_3 \rightarrow 5\ Cr_2O_3 + 9O$$

i.e., 904 g. of chromium chromate on heating affords 760 g. of chromic oxide. Therefore, the ratio between the weight of two molecules of chromium chromate and chromic oxide obtained from two molecules of chromium chromate is 904 : 760 as 1.189 : 1.

It is quite evident from the above table that except the first ratio, all the rest are fairly constant within the limits of experimental error. Most of the ratios obtained in the above table are in fair agreement with the ratio calculated on theoretical grounds.

The high and low values of the ratios can be explained. The high value is on account of the fact that when the amount of the hydrogen peroxide added is less than the corresponding volume of chromic acid taken, some chromic acid is left unchanged and the oxidation value is high, thus, yielding the ratios high. When hydrogen peroxide is added in large excess, some of it is left unchanged and goes with the aqueous layer. This unchanged hydrogen peroxide reduces chromate ions to trivalent chromium state, thus providing oxidation values low, which yields a low ratio.

TABLE II

H_2O_2.	Total Cr_2O_3. (From 10 c.c. of the solution). (II)	Cr_2O_3 by pptn. (III)	Ratio cf. II/III.	H_2O_2.	Total Cr_2O_3. (From 10 c.c. of the solution). (II)	Cr_2O_3 by pptn. (III)	Ratio of II/III.
20 c.c.	0.2272 g.	0.0804 g.	2.80	100 c.c.	0.1382 g.	0.0514 g.	2.60
30	0.1878	0.0648	2.80	110	0.1346	0.0540	2.49
40	0.1625	0.0630	2.57	120	0.1196	0.0472	2.50
50	0.1256	0.0520	2.40	140	0.1000	0.0450	2.20
60	0.1446	0.0602	2.40	160	0.1052	0.0842	2.10
70	0.1294	0.0525	2.40	180	0.0820	0.0420	2.10
80	0.1292	0.0564	2.30	200	0.0890	0.0444	2.00
90	0.1520	0.0572	2.60				

When two molecules of chromium chromate are precipitated by means of dilute solution of sodium hydroxide, the reaction is represented by the equation :

$$2\ Cr_2(CrO_4)_3 + 12\ NaOH = 4\ Cr(OH)_3 + 6\ Na_2CrO_4.$$

Further, when chromium hydroxide is ignited it is obtained as :

$$4\ Cr(OH)_3 = 2\ Cr_2O_3 + 6\ H_2O$$

i. e., the total weight of chromium oxide obtained from two molecules of chromic chromate is 760 g., and when precipitated, the weight of Cr_2O_3 is 304 g. Therefore the ratio between the total chromium oxide and the chromic oxide obtained from the basic part of the chromium is 760 : 304 as 2.5 : 1.

From Table II it is quite evident that most of the results are between 2.40 and 2.60, which are in fair agreement with the theoretical results calculated. The first few results are higher ; the reason is that on account of less amount of hydrogen peroxide added, the whole of the chromic acid taken is not completely acted upon, thus the value for the oxide obtained by the precipitation method is less. In the last portion

of the table the ratios are lower. The reason is that on account of too much excess of hydrogen peroxide, some of the chromate ions are reduced to hydrated chromic oxide which comes down as a precipitate of chromium hydroxide when NaOH is added. Thus, the amount of precipitated chromic hydroxide increases and it lowers the ratio.

It is clear from the above results that it is very likely that when the blue peroxychromic acid has been extracted out, the aqueous layer contains chromium chromate. When the layer is left for more than a week, it is precipitated.

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HETEROCYCLIC COMPOUNDS. PART XXXI. THE SYNTHESIS OF PARTIALLY METHYLATED ETHERS OF POLYHYDROXY COUMARINS

By R. D. Desai and (Miss) J. V. Parghi

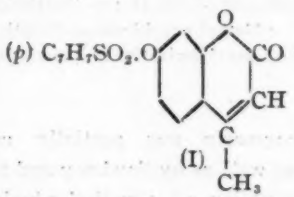
Partial tosylation of 4-methyl-5 :7-dihydroxycoumarin furnished 4-methyl-5-hydroxy-7-coumarinyl-*p*-toluenesulphonate which could be methylated to 4-methyl-5-methoxy-7-conmarinyl-*p*-toluenesulphonate. Its detosylation afforded 4-methyl-5-methoxy-7-hydroxycoumarin. Partial tosylation of 4-methyl-7 :8-dihydroxycoumarin provided 4-methyl-8-hydroxy-7-coumarinyl-*p*-toluenesulphonate; its methylation and subsequent detosylation yielded 4-methyl-7-hydroxy-8-methoxycoumarin, while the partial methylation of 4-methyl-7 :8-dihydroxyconmarin furnished the isomeric 4-methyl-7-methoxy-8-hydroxycoumarin. 5-Hydroxy-6-methoxy-4 :7-dimethylcoumarin was prepared by the alkaline persulphate oxidation of 5-*O*-mesyl derivative of 5-hydroxy-4 :7-dimethylcoumarin, followed by its methylation and subsequent demesylation. 4-Methyl-5 :7-dihydroxy-6-methoxycoumarin was prepared by the alkaline persulphate oxidation of di-*O*-mesyl derivative of 4-methyl-5 :7-dihydroxycoumarin, its methylation and subsequent demesylation.

4-Methyl-5 : 7-dihydroxycoumarin was partially methylated by Schmidt (*Helv. Chim. Acta*, 1947, **30**, 1661) as well as by Sawhney and Seshadri (*Proc. Ind. Acad. Sci.*, 1953, **37A**, 592) with the formation of 4-methyl-5-hydroxy-7-methoxycoumarin (m.p. 256-57°). We have found that partial tosylation of 4-methyl-5 : 7-dihydroxycoumarin furnishes 4-methyl-5-hydroxy-7-coumarinyl *p*-toluenesulphonate (I) which on methylation and subsequent detosylation of the methyl ether affords the isomeric 4-methyl-5-methoxy-7-hydroxycoumarin, m.p. 197°. Velluz and Amiard (*Bull. soc. chim.*, 1948, 1109) obtained 7-methoxy-6-hydroxy-4-methylcoumarin by the partial methylation of 6 : 7-dihydroxy-4-methylcoumarin. The synthesis of the isomeric 7-hydroxy-6 methoxy-4-methylcoumarin or 4-methylscopoletin from 6 : 7-dihydroxy-4 methylcoumarin by partial tosylation, methylation and detosylation has already been described in the previous paper (this *Journal*, 1956, **33**, 483).

The partial methylation of 4-methyl-7 : 8-dihydroxycoumarin does not seem to have been studied. On partial methylation with dimethyl sulphate and potassium carbonate in dry acetone, it afforded 4-methyl-7-methoxy-8-hydroxycoumarin (m.p. 145°), providing a yellow non-fluorescent solution in dilute alkali. The isomeric 4-methyl-7-hydroxy-8-methoxycoumarin, (m.p. 157°) which gave a blue fluorescent solution in dilute alkali, was prepared by the partial tosylation of 4-methyldaphnetin, which yielded 4-methyl-8-hydroxy-7-coumarinyl-*p*-toluenesulphonate (II), followed by its methylation and subsequent detosylation. Thus, in the case of dihydroxycoumarins whenever there is one hydroxyl group in 7-position and the other hydroxyl group in any other position (5, 6 or 8), methylation and tosylation affect preferentially position- 7 only. Our preliminary experiments on partial mesylation of polyhydroxy coumarins show similarity between tosylation and mesylation, but these experiments will form the subject of a further communication.

Miss Bhavsar and Desai (this *Journal*, 1954, **31**, 141) have prepared 5-hydroxy-6-methoxy-4 : 7-dimethylcoumarin (III) by the oxidation of 4 : 7-dimethyl-5-coumarinyl-*p*-toluenesulphonate with alkaline potassium persulphate, its methylation and subsequent detosylation. We have found that (III) can be prepared in an improved yield by the oxidation of 4 : 7-dimethyl-5-coumarinyl-methanesulphonate (IV) with alkaline potassium persulphate to 4 : 7 - dimethyl - 6-hydroxy - 5-coumarinyl - methanesulphonate (V), its methylation to 4 : 7 - dimethyl - 6-methoxy - 5-coumarinyl-methanesulphonate (VI) and subsequent demesylation.

Miss Bhavsar and Desai (*loc. cit.*) failed to oxidise 4-methyl-5 : 7-coumarinyl di-*p*-toluenesulphonate. This is due to the steric hindrance offered by the bulky tosyl groups, as we have now succeeded in oxidising 4-methyl-5:7 coumarinyl-dimethanesulphonate (VII) by alkaline potassium persulphate to 4 - methyl-6 - hydroxy - 5 : 7-coumarinyl-dimethanesulphonate (VIII) which on methylation and subsequent demesylation furnishes 4-methyl-5 : 7-dihydroxy-6-methoxycoumarin (IX).



(I)

EXPERIMENTAL

Monotosylation of 4-Methyl-5 : 7-dihydroxycoumarin and Formation of 4-Methyl-5-hydroxy-7-coumarinyl-p-toluenesulphonate (I)

A mixture of 4-methyl-5:7-dihydroxycoumarin (2 g.), *p*-toluenesulphonyl chloride (2 g.), acetone (50 c. c.) and anhydrous potassium carbonate (6 g.) in a round-bottomed flask was refluxed for 12 hours. After removal of the acetone, the solid was treated with 5% NaOH solution. The monotosylated derivative went in solution while the ditosylated product remained insoluble. On acidification with HCl (c nc.), monotosyl derivative (1.3 g.) was recovered. It crystallised from alcohol in white needles, m.p. 240°. It dissolved in alkali with a yellow colour and showed no fluorescence. (Found: S, 9.1. $C_{17}H_{14}O_6S$ requires S, 9.2 per cent).

4-Methyl-5-methoxy-7-coumarinyl-p-toluenesulphonate was obtained by refluxing the mixture of (I, 0.5 g.), anhydrous potassium carbonate (4 g.), dimethyl sulphate (2 g.) and anhydrous acetone (50 c. c.) for 12 hours. The residue left after removal of the acetone was treated with water. The insoluble product crystallised from alcohol in white plates, m.p. 188°. Its reddish brown solution in H_2SO_4 (conc.) showed a green fluorescence. (Found: S, 8.6. $C_{18}H_{16}O_6S$ requires S, 8.8 per cent).

4-Methyl-5-methoxy-7-hydroxycoumarin was prepared by pouring a solution of the preceding coumarin (0.5 g.) in H_2SO_4 (conc., 10 c.c.) in ice-cold water after 12 hours

and crystallised from ethyl acetate in white needles, m.p. 197°. It dissolved in alkali solution with a blue fluorescence. (Found : C, 64.3 ; H, 4.7. $C_{11}H_{10}O_4$ requires C, 64.1 ; H, 4.9 per cent).

Partial Methylation of 4-Methyl-7 : 8-dihydroxycoumarin and Formation of 4-Methyl-7-methoxy-8-hydroxycoumarin

A mixture of 4-methyl-7 : 8-dihydroxycoumarin (2 g.), dimethyl sulphate (1 c.c.), anhydrous potassium carbonate (3 g.) and acetone (30 c.c.) was refluxed on a water-bath for 12 hours. After removal of the acetone, the residue was treated with 5% NaOH solution. Acidification of the alkaline solution with concentrated hydrochloric acid gave a solid which crystallised from alcohol in white needles, m.p. 145°, depressed to 130° by admixture with a specimen of 4-methyl-7-hydroxy-8-methoxycoumarin, m.p. 157°, described hereunder. (Found : C, 64.0 ; H, 4.7. $C_{11}H_{10}O_4$ requires C, 64.1 ; H, 4.9 per cent). It dissolved in alkali solution with a yellow colour and no fluorescence, while its alcoholic solution developed a green coloration with ferric chloride.

4-Methyl-8-hydroxy-7-coumarinyl-p-toluenesulphonate (II) was prepared by refluxing a mixture of 4-methyl-7 : 8-dihydroxycoumarin (2 g.), *p*-toluenesulphonyl chloride (2 g.), anhydrous potassium carbonate (3 g.) and acetone for 12 hours, and worked up as usual. The monotosylated derivative (1.4 g.) crystallised from alcohol in white needles, m.p. 222°. It dissolved in alkali solution with a yellow colour and no fluorescence. Its alcoholic solution developed a green coloration with ferric chloride. (Found: S, 9.3. $C_{17}H_{14}O_6S$ requires S, 9.2 per cent).

4-Methyl-8-methoxy-7-coumarinyl-p-toluenesulphonate was prepared by heating a mixture of (II, 1 g.), dimethyl sulphate (5 c.c.), anhydrous potassium carbonate (10 g.) and acetone (75 c.c.) for 24 hours, and worked up as usual. It crystallised from alcohol in white needles, m.p. 148°. Its alcoholic solution showed no coloration with ferric chloride. (Found : S, 8.6. $C_{18}H_{16}O_6S$ requires S, 8.8 per cent).

4-Methyl-7-hydroxy-8-methoxycoumarin was obtained by pouring a solution of the preceding coumarin (0.5 g.) in H_2SO_4 (conc., 10 c.c.) in ice-cold water after 12 hours and crystallised from alcohol in white needles, m.p. 157°. It dissolved in alkali solution with a blue fluorescence, while its alcoholic solution gave no coloration with ferric chloride. (Found : C, 64.2 ; H, 4.6. $C_{11}H_{10}O_4$ requires C, 64.1 ; H, 4.9 per cent).

4 : 7-Dimethyl-5-coumarinyl-methanesulphonate (IV) was prepared by heating a mixture of 4:7-dimethyl-5-hydroxycoumarin (3.8 g.), methanesulphonyl chloride (2.5 g.), anhydrous potassium carbonate (10 g.) and acetone (50 c.c.) for 12 hours, and worked up as usual. It crystallised from alcohol in white thin needles, m.p. 198°. (Found : S, 11.8. $C_{12}H_{12}O_5S$ requires S, 11.9 per cent).

Oxidation of (IV) to *4 : 7-Dimethyl-6-hydroxy-5-coumarinyl-methanesulphonate* (V).—The oxidation of the solution of (IV, 2 g.) in pyridine (50 c.c.) was carried out by the gradual addition of the solution of KOH (4 g.) in water (40 c.c.) and potassium persulphate (4 g.) in water (100 c.c.), as described by Miss Bhavsar and Desai (*loc cit.*), in the case of the *-O*-tosyl analogue. The solid (0.4 g.) crystallised from alcohol in white

needles, m.p. 205°, and dissolved in alkali solution with a yellow colour and no fluorescence. (Found : S, 11.2. $C_{12}H_{12}O_6S$ requires S, 11.3 per cent).

4 : 7-*Dimethyl*-6-*methoxy*-5-*coumarinyl*-*methanesulphonate* (VI) was obtained by methylation of (V) with dimethyl sulphate in presence of anhydrous potassium carbonate and acetone as usual. It crystallised from alcohol in white needles, m. p. 202°. It was insoluble in dilute sodium hydroxide solution. (Found : S, 10.8. $C_{13}H_{14}O_6S$ requires S, 10.7 per cent).

4 : 7-*Dimethyl*-5-*hydroxy*-6-*methoxycoumarin* (III) was obtained by pouring the solution of (VI, 0.2 g.) in H_2SO_4 (conc., 5 c. c.) after 12 hours in ice-cold water and crystallised from ethyl acetate in white plates, m.p. 206°, undepressed by a sample prepared by Miss Bhavsar and Desai (*loc. cit.*).

4-*Methyl*-5 : 7-*coumarinyl*-*dimethanesulphonate* (VII) was prepared by refluxing a mixture of 4-methyl-5 : 7-dihydroxycoumarin (1.9 g.), methanesulphonyl chloride (2.5 g.), sodium bicarbonate (4 g.) and acetone (75 c.c.) for 6 hours, and purified as usual. It crystallised from alcohol in white needles, m.p. 173°. (Found : S, 18.5. $C_{12}H_{12}O_8S_2$ requires S, 18.4 per cent).

4-*Methyl*-6-*hydroxy*-5 : 7-*coumarinyl*-*dimethanesulphonate* (VIII) was prepared by the oxidation of (VII, 3.5 g.), dissolved in pyridine (50 c.c.), with a solution of KOH (9 g.) in water (90 c.c.) and potassium persulphate (8 g.) in water (200 c.c.). After working up the solution as usual, the solid (0.5 g.) crystallised from alcohol in white plates, m.p. 210°. It dissolved in alkali with a deep yellow colour. (Found : S, 17.4. $C_{12}H_{12}O_9S_2$ requires S, 17.5 per cent).

4-*Methyl*-6-*methoxy*-5 : 7-*coumarinyl*-*dimethanesulphonate* was obtained by methylation of (VIII) with dimethyl sulphate in presence of anhydrous potassium carbonate and acetone. It crystallised from dilute alcohol in white needles, m.p. 134°. (Found : S, 16.7. $C_{13}H_{14}O_9S_2$ requires S, 16.9 per cent).

4-*Methyl*-5 : 7-*dihydroxy*-6-*methoxycoumarin* (IX) was obtained by pouring a solution of the preceding coumarin (0.3) in H_2SO_4 (conc., 10 c.c.) after 12 hours in ice-cold water. It crystallised from alcohol in white needles, m.p. 230°. It was soluble in alkali solution with a deep yellow colour, and its alcoholic solution gave no coloration with ferric chloride. (Found : C, 59.2, H, 4.3. $C_{11}H_{10}O_5$ requires C, 59.5 ; H, 4.5 per cent).

4-*Methyl*-5 : 6 : 7-*trihydroxycoumarin* was obtained by pouring the solution of (VIII, 0.2 g.) in H_2SO_4 (conc., 5 c.c.) in ice-cold water after 12 hours. It crystallised from alcohol in white needles, m.p. 277°, undepressed by a sample prepared independently by Miss Bhavsar and Desai (*Ind. J. Phar.*, 1951, **13**, 200), Parikh and Sethna (this *Journal*, 1950, **27**, 369) and Sawhney, Seshadri and Thiruvengadam (*Proc. Ind. Acad. Sci.*, 1951, **33A**, 11).

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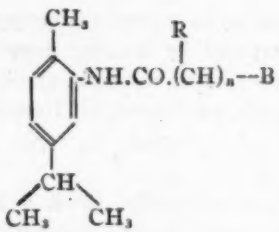
SEARCH FOR NEW LOCAL ANAESTHETICS. PART I

By I. Sen Gupta and Vasudev

Several diethylamino-, piperidino- and morpholino-acetyl and -propionyl derivatives of 2-methyl-5-*iso*propylaniline have been synthesised and their local anaesthetic activity studied.

Basic amides and basic anilides, like basic esters having lypolytic and hydrophilic moieties, show local anaesthetic activity (Miescher, *Ber.*, 1928, **61**, 730 ; Hoffer, *Klin. Woch.*, 1929, **8**, 1249; Lofgren, *Chem. Abs.*, 1937, **31**, 7854 ; Gaind *et al.*, this *Journal*, 1940, **17**, 400, 619). Strong local anaesthetic activity has been shown by basic anilides where lypolytic moiety is substituted by alkyl groups (Lofgren *et al.*, *Chem. Abs.*, 1948, **42**, 6378 ; 1949 **43**, 1021). Xylocaine (ω-diethylamino-2 : 6-dimethylacetanilide), reported by Lofgren *et al.* (*loc. cit.*), has been found to possess a very high local anaesthetic potency, both in surface as well as in infiltration anaesthesia, without much toxicity. It appears that the increase in number of alkyl groups raises the activity of the compounds. No attempt appears to have been made to substitute the lypolytic moiety with higher alkyl groups. With this object in view, compounds of the general type (I) have been synthesised for studying the local anaesthetic activity.



R = H or CH_3.

n = 1 or 2.

B = Dimethylamino, piperidino or morpholino.

(I)

These compounds were synthesised by chloro-acylation of 2-methyl-5-*iso*propylaniline with chloroacetyl chloride, α-chloropropionyl chloride and β-chloropropionyl chloride. 2-Methyl-5-*iso*propylaniline was prepared in better yields by nitrating *p*-cymene ("Org. Synthesis", 1941, **21**, 96), followed by reduction of the nitro compound (Wheeler and Smithey, *J. Amer. Chem. Soc.*, 1921, **43**, 2613). The chloro-acetylated product was then condensed with the secondary amine. The bases being liquid were characterised through their solid derivatives.

Experimental

*ω-Chloroacetyl-2-methyl-5-*iso*propylaniline* (I : R = H; n = 1 ; B = Cl).—Chloroacetyl chloride (13.5 g.) in dry benzene (20 c.c.) was gradually added to 2-methyl-5-*iso*propylaniline (14.9 g.) in dry benzene (20 c.c.). The mixture was refluxed on a water-bath for an hour. Benzene was distilled off and the residue washed with water,

followed by sodium bicarbonate solution. The chloro-acetylated product on chilling in ice came out as a white solid which was crystallised from 80% alcohol and then recrystallised from petroleum ether (b.p. 60°-80°) in small needles, m.p. 84°, yield 13.5 g. (Found : N, 6.5. $C_{12}H_{16}ONCl$ requires N, 6.2 per cent).

Hydrochloride of N-*Piperidinoacetyl-2-methyl*-5-iso*propylaniline* (I : R = H ; n = 1 ; B = piperidino).—A mixture of the above chloro compound (2.3 g.) and piperidine (1.7 g.) in absolute alcohol (20 c.c.) was refluxed for 4 hours. Alcohol was distilled off and the residue treated with sodium bicarbonate solution. It was then dissolved in dilute hydrochloric acid, filtered and again basified to liberate the base. The oily base was extracted with ether and converted into its hydrochloride. The hydrochloride was crystallised from dry acetone - dry petroleum ether (b.p. 60°-80°) mixture, m. p. 189°. (Found : N, 8.8 ; Cl, 11.5. $C_{17}H_{26}ON_2.HCl$ requires N, 9.01; Cl, 11.43 per cent).

Perchlorate of diethylaminoacetyl-2-methyl-5-iso*propylaniline* (I : R = H ; n = 1 ; B = diethylamino) was prepared in a similar manner by heating the chloro compound (2.3 g.) and diethylamine (1.5 g.) in absolute alcohol. The base and also its hydrochloride came out to be sticky masses which could not be purified. The base was therefore extracted with ether and to the ethereal extract a few drops of perchloric acid added. The solution was triturated thoroughly when a solid mass separated. It was crystallised from acetone, m.p. 234° (decomp.). (Found ; N, 7.4. $C_{16}H_{26}ON_2.HClO_4$ requires N, 7.7 per cent).

Hydrochloride of N-*morpholinoacetyl-2-methyl*-5-iso*propylaniline* (I : R = H ; n = 1 ; B = morpholino) was similarly prepared by heating morpholine (1.8 g.) with the chloro compound (2.3 g.). The base came out to be an oil which was converted into its hydrochloride. The hydrochloride was crystallised from dry acetone- dry petroleum ether (b.p. 40°-60°) mixture, m.p. 150°. (Found : N, 8.79. $C_{16}H_{24}O_2N_2.HCl$ requires N, 8.96 per cent).

β-*Chloropropionyl-2-methyl*-5-iso*propylaniline* (I : R = H ; n = 2 ; B = Cl) was obtained by treating 2-methyl-5-*iso*propylaniline (14.9 g.) with β-chloropropionyl chloride (15.2 g.) in the usual way. It came out to be an oily substance and therefore it was distilled under vacuum. The product distilling at 198°-200°/5-7 mm. was collected (9.5 g.).

Hydrochloride of β-N-*piperidinopropionyl-2-methyl*-5-iso*propylaniline* (I : R = H; n = 2 ; B = piperidino) was prepared by refluxing a mixture of piperidine (1.7 g.) and the chloro compound (2.4 g.) in absolute alcohol for 5 hours. The base, an oily substance, was isolated in an analogous manner. It was converted into its hydrochloride in the usual way and the hydrochloride crystallised from dry acetone in white needles, m.p. 104°. (Found : N, 8.3. $C_{18}H_{28}ON_2.HCl$ requires N, 8.62 per cent).

β-*Diethylaminopropionyl-2-methyl*-5-iso*propylaniline Picrate* (I : R = H ; n = 2 ; B = diethylamino).—The base was prepared by heating diethylamine (1.5 g.) and the foregoing chloro compound (2.4 g.) in absolute alcohol. The base was an oily substance and its hydrochloride was also found to be hygroscopic. It was therefore converted into its picrate in benzene solution and the picrate was crystallised from benzene, m.p. 96-97°. (Found : N, 13.2. $C_{17}H_{28}ON_2.C_6H_3O_7N_3$ requires N, 13.8 per cent).

α-Chloropropionyl-2-methyl-5-isopropylaniline (I : R = CH_3 ; n = 1 ; B = Cl) was obtained by treating 2-methyl-5-*iso*propylaniline (14.9 g.) with α-chloropropionyl chloride (15.2 g.) in the usual way. The product was crystallised from petroleum ether (b. p. 60°-80°) in needles (11.0 g.), m.p. 74°. (Found : N, 5.65. $C_{13}H_{16}ONCl$ requires N, 5.84 per cent).

Perchlorate of α-N-piperidinopropionyl-2-methyl-5-isopropylaniline (I : R = CH_3 ; n = 1 ; B = piperidino) was prepared in an analogous manner by heating the foregoing chloro compound (2.4 g.) with piperidine (1.7 g.). The base came out to be a semi-solid mass and its hydrochloride was also found to be sticky which could not be crystallised. The perchlorate of the base was prepared in the usual way and crystallised from absolute alcohol-ether mixture in white needles, m.p. 158°. (Found : N, 7.8. $C_{18}H_{28}ON_2.HClO_4$ requires N, 7.2 per cent).

The preliminary investigations on the local anaesthetic activity of the hydrochloride of N-piperidinoacetyl-2-methyl-5-*iso*propylaniline in 2% solution shows better surface anaesthesia (42 minutes) on rabbit cornea than cocaine (38 minutes) in 2% solution. Hydrochloride of β-N-piperidinopropionyl-2-methyl-5-*iso*propylaniline shows lesser activity than the acetyl analogue. The compounds are being studied further for their pharmacological activity.

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ACTION OF SULPHUR DIOXIDE WATER ON AMMONIUM PERMANGANATE

By Kundan Lal and Chander Mehra

The action of sulphur dioxide water (sulphurous acid) on ammonium permanganate tends to the formation of a dark brown precipitate of the general composition: x $(NH_4)_2O$, y MnO, z MnO_2. The filtrate shows distinctly acidic reactions due to the presence of sulphuric acid formed during the reaction. Ammonium sulphate, manganese sulphate and ammonium dithionate are the various products of reaction.

The dark brown precipitate, when sulphurous acid is further added, is completely redissolved, the reaction at this stage being represented by the equation :

$$14(NH_4)MnO_4 + 37\ H_2SO_3 = 2\ (NH_4)_2S_2O_6 + 5\ (NH_4)_2SO_4 + 14\ MnSO_4 + 14\ H_2SO_4 + 23\ H_2O.$$

In a previous communication (Lal and Singh, this *Journal*, 1955, **32**, 547) the action of sulphurous acid on calcium permanganate has been reported. The present work includes the study of the action of sulphurous acid on ammonium permanganate.

Experimental

Ammonium permanganate was prepared by dissolving $KMnO_4$ of A.R. quality (16 g.) in distilled water (300 c.c.) at 70° and mixing it with a solution of NH_4Cl (A.R., 44 g.) in distilled water (300 c.c.), and concentrating the volume to about 200 c.c. It was cooled to 0° with ice, when long needle-shaped crystals of ammonium permanganate were obtained which were filtered in a sintered glass crucible, washed with distilled water three to four times and recrystallised from distilled water thrice (Moles and Crespi, *Anales Soc. espan. Fis. quim.*, 1922, **20**, 555). These crystals without drying were dissolved in water and made up to a known volume. On qualitative analysis the solution was found to be free from K^+ and Cl^-. The purity was further tested by determining MnO_4^- by titrating against a standard solution of ferrous ammonium sulphate (A.R.), and NH_4^+ by Kjeldahl's method (Swift, "A System of Chemical Analysis", 1940, pp. 404-406). Both these values agreed with the formula $(NH_4)MnO_4$ within 0.5% error. For each duplicate set, a fresh sample of ammonium permanganate was prepared, analysed and diluted to make it 0.5% solution likewise.

Sulphur dioxide gas was prepared by dropping H_2SO_4 (dil.) on potassium bisulphite. Sulphurous acid was prepared by bubbling this gas through a dark coloured ground-glass stoppered bottle filled with distilled water to the brim and surrounded by ice. It was titrated against a standard alkali solution quickly and then diluted with distilled water till it was normal (approx.). To have comparatively the same strength of the acid, a fresh sample was prepared every time. The oxidation of sulphur dioxide in solution was avoided by protecting it from direct exposure and by conducting the whole experiment in the shortest possible time. Some loss of sulphur dioxide due to volatilisation was always unavoidable, but no sulphate formation was detected in the sample of sulphurous acid.

The normal sulphurous acid, thus prepared, was added dropwise from the burette to ammonium permanganate solution (100 c.c., 0.5%), taken in two separate beakers, till the pink colour was just discharged. The precipitate at this stage of the reaction, *i.e.* the intermediate stage, after separating from the filtrate, was found to contain manganese dioxide, manganous oxide and ammonia. Presence of any sulphur acid was not detected in the precipitate. The oxides of manganese were determined by the methods used by Lal and Singh (*loc. cit.*) and ammonia by Kjeldahl's method. The analytical results (Table I) indicate the molar ratio between $(NH_4)_2O$, MnO and MnO_2 as 1 : 1 : 7.

The filtrate indicated the presence of NH_4^+, SO_4^{2-}, $S_2O_6^{2-}$ and H_2SO_4. Traces of Mn^{2+} were also suspected in the filtrate. NH_4^+ was estimated by Kjeldahl's method and the rest of the reaction products by the methods used previously. In the filtrate, which was acidic, NH_4^+ was accounted for as SO_4^{2-} and $S_2O_6^{2-}$. The Mn^{2+} content of the filtrate was very small and was determined by difference.

The decolorisation stage of the reaction was studied with the increasing volumes of normal sulphurous acid. The various analytical values are recorded in Table I. In the final stage (Expt. No. 6) NH_4^+ was accounted for both as sulphate and dithionate, and Mn^{2+} as sulphate only.

To study the preliminary stage of the reaction, more experiments in duplicate were repeated with three-fourth and half of the volume of sulphurous acid required for the intermediate stage. The amounts of various reaction products and the percentage decomposition of ammonium permanganate are shown in Table I.

TABLE I

Total Mn^{2+} added = 0.2007 g. Total NH_4^+ added = 0.0657 g.

1	2	3	4	5	6	7	8
			Filtrate				Precipitate
Expt. No.	H_2SO_3 added.	NH_4MnO_4 decomp.	$(NH_4)_2SO_4$.	$(NH_4)_2S_2O_6$.	$MnSO_4$.	H_2SO_4.	$(NH_4)_2O$: MnO : MnO_2 (mol. ratio).
1	6.00 c.c.	54.84%	0.11086 g.	0.00349 g.	Nil	0.1438 g.	1 : 2.43 : 10 09
	6.00	54 64	0.11056	0.004012		0.1445	1 : 2.30 : 9.88
2	9 00	77.32	0.1386	0.00546	,,	0.2934	1 : 1.39 : 7.06
	9.00	77.23	0.1368	0.00638		0.2934	1 : 1.34 : 6.86
3	12.10	100	0.1741	0.00786	0.00586 g.	0.3875	1 : 1.16 : 6.55
	12.10		0.17724	0.00795	0 00604	0.3865	1 : 1.33 : 7.23
4	14 60	,,	0.1745	0.0518	0.08648	0 4060	1 : 2.75 : 9 65
	14.60		0 1734	0.05396	0.08782	0'4037	1 : 2.94 : 10.17
5	17.10	,,	0 17485	0 08723	0.1992	0.3967	1 : 13.24 : 20.52
	17 10		0.17456	0.08581	0.2018	0.3990	1 : 12.59 : 20 86
6	21.40	,,	0.17384	0.10082	0.5510	0.3453	Nil
	21.40		0.17479	0.09942	0.5510	0.3453	

DISCUSSION

About 89% of sulphurous acid added is converted into other sulphur acids (SO_4^{2-} and $S_2O_6^{2-}$) and the rest is lost by volatilisation during the preparation and addition of sul

phurous acid. Regarding the formation of various sulphur acids in the filtrate, the results are in agreement with those already obtained when normal sulphurous acid is allowed to react with calcium permanganate solution (*loc.cit.*). In the final stage (Expt. No. 6), the reaction is represented as

$$14\ NH_4MnO_4 + 37\ H_2SO_3 = 2\ (NH_4)_2\ S_2O_6 + 5\ (NH_4)_2SO_4 + 14\ MnSO_4 + 14\ H_2SO_4 + 23\ H_2O.$$

The value of the mol. ratio $(NH_4)_2O$: MnO : MnO_2 in the intermediate stage is 1 : 1: 7 as against 1.2 : 13 in the case of calcium permanganate ($CaO, 2MnO, 13MnO_2$). A similar complex is formed in Expt. 2 while the composition changes to 1 : 3 : 10 and 1:13 : 21 in Expts. 4 and 5. The difference between the calcium and the ammonium complexes in the corresponding stages is probably due to their different basic character.

According to Biltz (*Gott. Nachr.*, 1930, 189) hydrated manganese dioxide may be regarded as permanganous acid, H_2MnO_3, so that manganese dioxide becomes permanganous anhydride, and the salts RO. $nMnO_2$, permanganites. According to Groger (*Ann. chim. phys.*, 1862, *iii*, **66**, 161) these permanganites may be regarded as the various derivatives of hydrated manganese dioxide.

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CHEMOTHERAPEUTIC DYES: SYNTHESIS OF SUBSTITUTED AMINOPHENOXAZINES

By A. B. Sen and R. C. Sharma

Several 5-β-hydroxyethylamino-9-di(mono)alkylaminobenzo(a)phenoxazines and phenyl or *tert.*-butylaminophenoxazines have been prepared as potential tumor inhibiting and antitubercular agents.

The basic dyes, Nile Blue A and Nile Blue 2B, containing a benzo (a) phenoxazonium nucleus, have been found to possess a selective tumor staining and growth retarding action (Lewis *et al.*, *Anat. Record*, 1946, **95**, 89; 1946, **98**, 201; 1947, **99**, 369), and as such are of potential importance as diagnostic and therapeutic agents in the study of cancer. New methylene blue GG, a phenoxazine derivative, was found (de Witts, *J. Inf. Dis.*, 1913, **13**, 378) to stain tubercle bacillus in *vitro* and penetrate the tubercle in *vivo*. These findings led Okomoto (*Jap. Med. J.*, 1948, 1422; *Chem. Abs.*, 1951, **45**, 5757), Crossley *et al.* (*J. Amer. Chem. Soc.*, 1952, **74**, 573; *Chem. Abs.*, 1955, 2085), and Clapp *et al.* (*J. Amer. Chem. Soc.*, 1952, **74**, 1989) to synthesise derivatives of phenoxazines, with a view to studying the effects of structural modifications on these actions, and the toxicity of the compound to the host.

Crossley *et al.* (*loc. cit.*) studied three series of these compounds, viz., (*a*) 5-aralkylamino-9-alkylamino-, (*b*) 5-arylamino-9-dialkylamino-, and (*c*) 5-heterocylic amino-9-dialkylamino-benzo(a)phenoxazines and found that the compounds of the second series were of the greatest importance, whilst those of the first series possessed some activity, and those of the third were without significant activity.

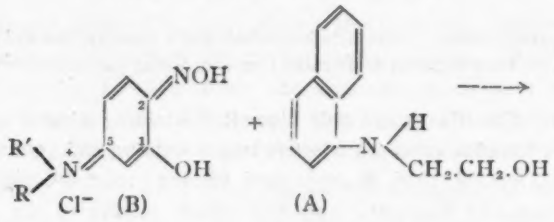
Clapp *et al.* (*loc. cit.*) extended this work by synthesising aminobenzo(a) phenoxazines containing (*i*) a methyl group in position-6, (*ii*) a chlorine atom in position-10, (*iii*) 5-arylamino-9-arylamino groupings, and found that the substitution in 6 and 10 positions always lowered the activity of the parent compound; removal of the benzo ring or of 9-dialkylamino substituent also resulted in the lowering of the activity.

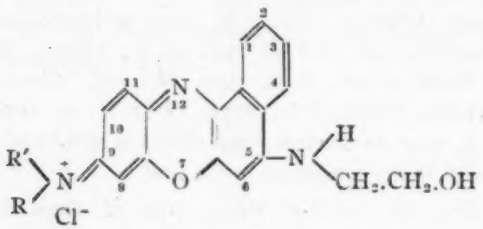
The present work was undertaken to study other variations in the structure of these dyes.

The difference in the potency of therapeutically active compounds of varying fat/water solubility coefficients arises out of the difference in the distribution of the drug between the aqueous phase of the tissue fluids, through which the drug must pass to reach the site of infection, and the infected tissues in which the drug molecules combine with bioreceptors. Since the cell membrane of mycobacteria and to some extent the tissues that harbour them are rich in lipoid material, the drug should also possess sufficient lipoid solubility so as to pass through these tissues and kill the bacteria. For this purpose, benzo(a)phenoxazines, having alkylamino groups for lipoid solubility in position-9 and a β-hydroxyethylamino grouping in position-5, were synthesised to confer partial water solubility.

In addition to these, some simple aminophenoxazines with phenyl and *tert.*-butyl substituents have been prepared as the investigations of Boothroyd *et al.* (*J. Chem. Soc.*, 1953, 1499) have established that 1-amino- and 3-aminophenoxazines possess marked tuberculostatic activity.

5-β-Hydroxyethylamino-9-dialkylamino-benzo(a)phenoxazonium chlorides have been prepared by the following reaction :



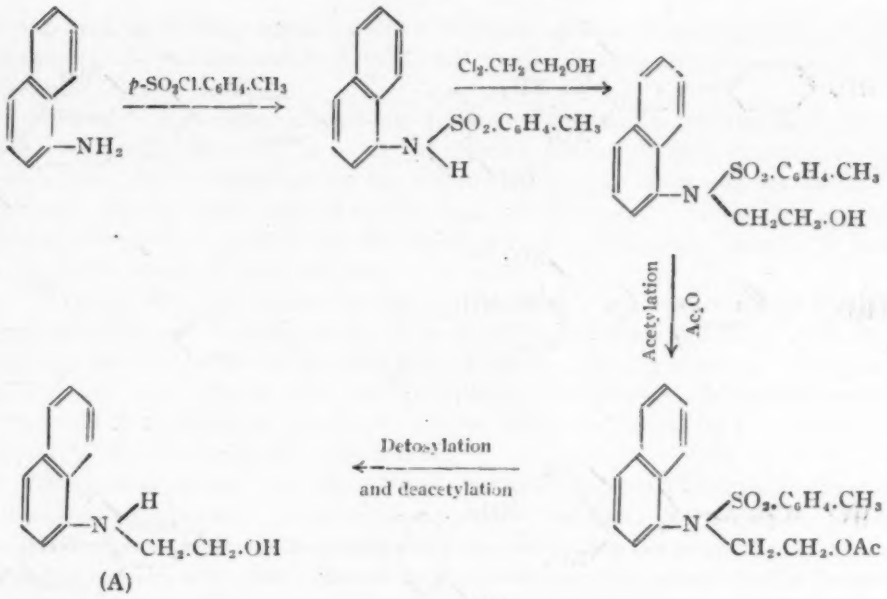


[I : R = R′ = Me. II : R = Et ; R′ = H. III : R = R′ = Pr. IV : R = R′ = C_4H_9. V : R = R′ = C_5H_{11}. VI : R = R′ = C_6H_{13}.]

Of these dyes, (IV) and (V) could not be isolated from the final reaction mixture which was in the form of a dark green syrup and as such could not be characterised. Other dyes were quite similar to 5-aralkylamino-9-dialkylamino-benzo(a)phenoxazonium chlorides (Crossley *et al.*, *loc. cit.*), being dark green crystalline solids which imparted blue colour in acidic medium and red colour in basic medium, which is the characteristic of the series. They also formed precipitates with silver nitrate solution. These dyes, for most part, did not show satisfactory melting or decomposition points, and hence, were characterised as picrates which could easily be obtained in the pure state.

α-Naphthyl-(N-β-hydroxyethyl)-amine, (A), required in the above condensation, was prepared from α-naphthylamine by a method analogous to one adopted by Nityanand *et al.* (*J. Sci. Ind. Res.*, 1954, **13B**, 260) for the synthesies of *p*-(ω-hydroxyalkylamino)-*p*-aminodiphenylsulphones.

The necessary 3-monoalkyl- and 3-dialkylaminophenols were prepared from 3-aminophenols by alkylation with appropriate alkyl iodide. They were converted into the corresponding 5-mono- and dialkylamino-2-nitrosophenol hydrochlorides (B) by the same technique as described by Crossley *et al.* (*loc. cit.*).



(A)

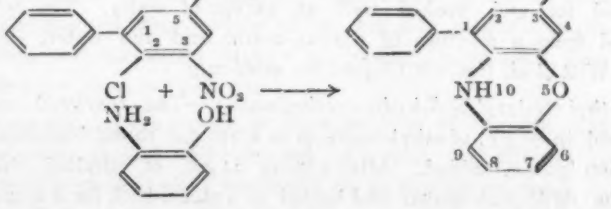
The benzo(a)phenoxazonium salts were prepared by the condensation of (A) and (B) in absolute alcohol medium instead of ordinary alcohol because of the hydrophilic grouping in (A), following the method A of Crossley *et al.* (*loc. cit.*).

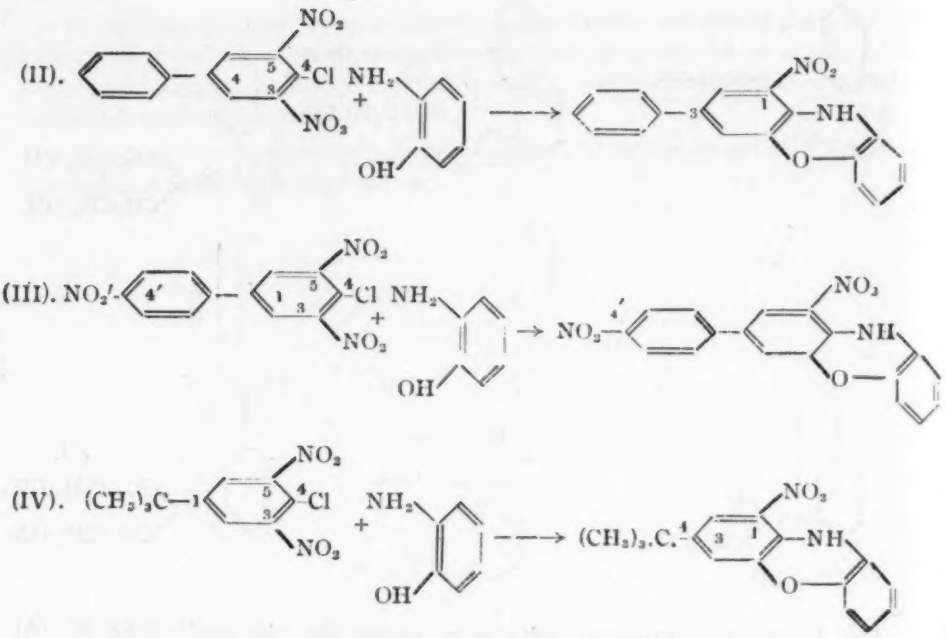
Picrates of these dyes were prepared from the free bases as recorded in the Experimental.

The aminophenoxazines were prepared by the catalytic reduction of the nitrophenoxazines using Adams' catalyst and acetic acid. The bases were isolated in their oxidised from as imine hydrochlorides. The absence of amino groups was indicated by the inabilty to form a diazo compound. Purification of these dyes by reprecipitation or recrystallisation failed to remove a small amount of water-insoluble material. As such they were also characterised through their picrates.

The four nitrophenoxazines were obtained by the condensation of *o*-aminophenol with 2-chloro-3 : 5-dinitrodiphenyl, 4-chloro-3 : 5-dinitrodiphenyl, 4-chloro-3:5:4′-trinitrodiphenyl and 4-chloro-3:5-dinitro-1-*tert.*-butylbenzene respectively, as represented below:

(I).





The chloro compounds were obtained from the corresponding nitrophenols and phosphorus oxychloride in presence of diethylaniline.

3 : 5-Dinitro-2-oxydiphenyl (Borsche, *Annalen.*, 1900, **312**, 226), 3 : 5-dinitro-4-oxydiphenyl (Latschinoff, *Ber.*, 1873, **6**, 195), 3 : 5 : 4′-trinitro-4-oxydiphenyl (Garcia Banus *et al.*, *Anal. Fis. Quim.*, 1923, 126) and 3 : 5-dinitro-4-oxy-1-*tert.*-butylbenzene (Arthuestuder, *Annalen*, 1882, **211**, 244), needed in the above preparations, were obtained by the nitration of *o*- and *p*-diphenyls and *p*-*tert.*-butylphenol respectively.

EXPERIMENTAL

Aminobenzo(a)phenoxazines

α-Naphthyl(N-tosyl)amine was prepared by an improved method other than the one reported by Witt and Schemitt (*Ber.*, 1894, **27**, 2371). α-Naphthylamine (1 *M*) was dissolved in the minimum amount of pyridine and *p*-toluenesulphonyl chloride (1 *M*) was added to it. The mixture after being refluxed for 20 minutes was poured over crushed ice and washed with an excess of water. The solid obtained was recrystallised from a mixture of glacial acetic acid and water, m.p. 157°, yield theoretical. Witt *et al.* (*loc. cit.*) report the same m.p. .

α-Naphthyl (N-tosyl-N-β-hydroxyethyl)amine.—The tosylated compound (18 g.) was dissolved in 80 c.c. of ethyleneglycol in a 250 c.c. round bottomed flask and a 20% KOH solution (50 c.c.) added. After adding 24 c.c. of ethylene chlorohydrin to the mixture, the flask was sealed and heated in a steam-bath for 8 hours. The flask was then cooled and the contents poured over ice. The pink, plastic-like mass solidified on

cooling and on rubbing with a few drops of alcohol. On recrystallisation from alcohol pinkish crystals were obtained, m.p. 108°, yield 18 g. (Found: N, 3.92. $C_{19}H_{19}O_4NS$ requires N, 4.11 per cent).

α-Naphthyl (N-β-acetoxyethyl-N-tosyl) amine was obtained by refluxing the hydroxy compound (16 g.), dissolved in 25 c.c. of pyridine, with 36 c.c. of acetic anhydride for half an hour. The reaction mixture was poured over ice and washed with an excess of ice water. The oily residue solidified after about 2 hours' cooling. It was then recrystallised from alcohol in lustrous pinkish needles, m.p. 92°, yield 24 g. (Found: N, 4.02. $C_{21}H_{21}O_4NS$ requires N, 3.65 per cent).

α-Naphthyl(N-β-hydroxyethyl)amine.— Detosylation and deacetylation of the above compound was simultaneously effected by heating the compound (20 g.) with HCl (conc., 36 c.c.) and 50 c.c. of alcohol in a sealed vessel at 100° for 8 hours. The cooled solution was made alkaline with ammonium hydroxide and the crude reaction product recrystallised from alcohol as light pink crystals, m.p. 122°, yield 15.5 g. (Found: N, 7.15. $C_{12}H_{13}ON$ requires N, 7.49 per cent).

Dialkylaminophenols and their Nitroso-hydrochlorides.—3-Dimethylaminophenol, 3-di-*n*-propylaminophenol, 3-di-*n*-butylaminophenol, 3-di-*n*-amylaminophenol, 3-di-*n*-hexylaminophenol and their nitroso-hydrochlorides, required in the preparation of benzo-(a) phenoxazonium salts, were prepared in exactly the same way as described by Crossley *et al.* (*loc.cit.*) except that alkyl iodides were used for alkylation. The boiling points of the syrupy alkylaminophenols were almost identical with those given in the literature and their identity was confirmed by preparing their nitroso-hydrochlorides which had melting or decomposition points in agreement with the figures recorded in the literature.

5-Monoethylamino-2-nitrosophenol hydrochloride was obtained by the Fischer-Hepp rearrangement (*Ber.*, 1886, **19**, 2991) of *N*-nitroso-3-ethylaminophenol, prepared by the nitrosation of 3-ethylaminophenol. Its decomposition point (175°-180°) was also found to be correct.

The nitroso derivatives of 3-di-*n*-butylaminophenol and 3-di-*n*-amylaminophenol could not be isolated, and hence, the orange reaction solutions were directly used in the condensations.

Benzo(a)phenoxazonium Salts

5-β-Hydroxyethylamino-9-dimethylaminobenzo(a)phenoxazonium Chloride (I).—To a suspension of α-naphthyl(N-β-hydroxyethyl)amine (3.7 g., 0.02 *M*) in 24 c. c. of absolute ethanol were added 5-dimethylamino-2-nitrosophenol hydrochloride (6 g., 0.03*M*) and 0.5 c.c. of HCl (conc.), and the mixture was refluxed on a steam-bath under stirring for 3 hours. The original orange colour of the reaction mixture gradually darkened, changed to green and ultimately blue. On cooling the solution, dark green lustrous crystals separated out, m.p. 118-20°, yield 4 g.

For the preparation of the picrate, aqueous solution of the dye was basified with ammonium hydroxide (conc.) and extracted with ether. To the dry extract saturated ethereal solution of picric acid (dry) was added till no further precipitation. The picrate was obtained in yellow shining crystals in almost theoretical yield. In view of the sharp

melting point and shining crystalline form of the picrate, further purification by recrystallisation was considered unnecessary, m.p. 184°.

The picrate obtained was identified as (5:9)dipicrate of 5-β-hydroxyethylamino-9-dimethylaminobenzo(a)phenoxazine. [Found: N, 15.38. $C_{20}H_{20}O_2N_3$. $(C_6H_3O_7N_3)_2$ requires N, 15 91 per cent].

5-β - Hydroxyethylamino- 9 -ethylaminobenzo(a)phenoxazonium Chloride (II)..—The condensation was carried out under exactly similar conditions as given in the previous case by treating the naphthylamine derivative (3.7 g., 0.02 *M*) in 24 c.c. absolute ethanol with 5-ethylamino-2-nitrosophenol hydrochloride (6 g., 0.03 *M*) in the presence of HCl (conc., 0.5 c.c.). In the reaction mixture the same colour changes were observed, and on cooling, a solid of dark bluish green colour separated out. It decomposed above 150°, yield 3.8 g.

The dye was subsequently converted into the picrate, 5-β-hydroxyethylamino-9-ethylaminobenzo(a)phenoxazine (5:9) dipicrate, in the same way from the free base, in green shining crystals, m.p. 205°. [Found: N, 16.20. $C_{20}H_{20}O_2N_3$. $(C_6H_3O_7N_3)_2$ requires N, 15.91 per cent).

5-β-Hydroxyethylamino-9-di-n-propylaminobenzo(a)phenoxazonium Chloride (III). —This condensation was carried out exactly as above with α-naphthylamino compound and 5-di-*n*-propylamino-2-nitrosophenol hydrochloride. Under similar conditions, shinning dark green crystals separated out which melted sharply at 152°, yield 4.2 g.

The base obtained from the salt was converted into 5-β-hydroxyethylamino-9-di-*n*-propylaminobenzo(a)phenoxazine (5:9) dipicrate, by the same technique, in bottle-green shining crystals, m.p. 194°. [Found: N, 14.43. $C_{24}H_{28}O_2N_3$. $(C_6H_3O_7N_3)_2$ requires N, 14.85 per cent].

5-β-Hydroxyethylamino-9-di-n-butylaminobenzo(a)phenoxazonium Chloride (IV).— As 5-di-*n*-butylamino-2-nitrosophenol hydrochloride could not be isolated in the solid state, the orange reaction solution, obtained by the nitrosation of 3-di-*n*-butylaminophenol (10 g., 0.05 *M*) was added to a suspension of the naphthylamine derivative (3.7 g., 0.02 *M*) in 24 c.c. absolute ethanol along with HCl (conc., 0.5 c.c.). By the usual treatment, the mixture turned into a dark green syrup from which the dye could not be separated out even on cooling in the freezing mixture. Slow evaporation of the alcoholic solution ultimately left a dark green mass which could not be worked out and as such the dye could not be characterised.

5-β-Hydroxyethylamino-9-di-n-amylaminobenzo(a)phenoxazonium Chloride (V).— Same difficulty was observed in the isolation of this dye as the entire reaction solution obtained by the nitrosation of 3-di-*n*-amylaminophenol (12.5 g., 0.05 *M*) had to be added to naphthylamine derivative (3.7 g., 0.02 *M*) in 24 c.c. of absolute ethanol containing HCl (conc., 0.5 c.c.). The final reaction mixture was again a dark green syrup. Slow evaporation of the alcoholic solution left a similar dark green mass which could not be identified.

5-β-Hydroxyethylamino-9-di-n-hexylaminobenzo(a)phenoxazonium Chloride (VI). —5-Di-*n*-hexylamino-2-nitroso hydrochloride (10 g., 0.03 *M*) was added to a suspension of naphthylamine derivative (3.7 g., 0.02 *M*) in 24 c.c. absolute ethanol followed, by HCl

(conc., 0.5 c.c.). After refluxing for 3½ hours under stirring, a dark green solution was obtained which afforded a crystalline solid of the same colour on cooling, m.p. above 130° (not sharp), yield 4.5 g.

The picrate was obtained from the dye in the usual way in bottle-green crystals [5-*β*-hydroxyethylamino-9-di-*n*-hexylaminobenzo (a) phenoxazine 5 : 9- dipicrate], m.p. > 300°. (Found : N, 13.82. $C_{30}H_{40}O_2N_3$. $(C_6H_3O_7N_3)_2$ requires N, 13.52 per cent).

Aminophenoxazines

2-Chloro-3 : 5-dinitrodiphenyl was obtained in about 80% yield by treating 2-oxy-3 : 5-dinitrophenyl (8 g.) with $POCl_3$ (30 c.c.) and diethylaniline (8 c.c.) in the usual way, m.p. 119°.

4-Chloro-3 : 5-dinitrodiphenyl was obtained from 4-oxy 3 : 5 dinitrodiphenyl by treating with the same proportions of $POCl_3$ and diethylaniline, m.p. 150-51°.

4-Chloro-3 : 5 : 4′-trinitrodiphenyl was obtained in almost theoretical yield on treatment of 4-oxy-3 : 5 : 4′-trinitrodiphenyl with $POCl_3$ and diethylaniline, m.p. 171°.

4-Chloro-3 : 5-dinitro-1-tert.-butylbenzene was prepared from 4-oxy-3 : 5-dinitro-1-*tert.*-butylbenzene, diethyaniline and $POCl_3$ in the usual way, m.p. 115-16°.

(I). *1-Phenyl-3-nitrophenoxazine.*—*o*-Aminophenol (1.5 g.) and 2-chloro-3 : 5-dinitrodiphenyl (3.6 g.) were dissolved in 15 c.c. of alcohol and 2*N* sodium acetate solution (6 c.c., approx.) added. The mixture was refluxed under stirring for 5 hours and then 2*N*-NaOH (*ca.* 10 c.c.) was slowly added to the boiling mixture. The solution turned red and it was boiled for 30 minutes more. On allowing it to cool overnight, a dark brown product separated out, which was washed with dilute NaOH solution, followed by ethanol. Recrystallisation from *o*-xylene yielded fine reddish brown crystals (4 g.), m.p. 212°. (Found : N, 9.56. $C_{18}H_{12}O_3N_2$ requires N, 9.21 per cent).

(II). *3-Phenyl-1-nitrophenoxazine.*—4-Chloro-3 : 5-dinitrodiphenyl (3.6 g.), *o*-aminophenol (1.5 g.) in 2*N* sodium acetate (*ca.* 8 c.c.) and alcohol (15 c.c.) were stirred and heated under reflux for 4 hours. 2*N*-NaOH (*ca.* 10 c.c.) was then added. The mixture was boiled for half an hour more and set aside overnight. The dark brown solid obtained (3.8 g.), after washing with dilute NaOH solution and alcohol, was recrystallised from toluene in dark brown needles, m.p. 200°. (Found : N, 9.48. $C_{18}H_{12}O_3N_2$ requires N, 9.21 per cent).

(III). *3-(4′-Nitrophenyl)-1-nitrophenoxazine.*—4-Chloro-3.5:4′-trinitrodiphenyl (4.2 g.), when treated with similar proportions of *o*-aminophenol and NaOH in the medium of alcohol and sodium acetate solution, as described in the previous cases, yielded a brown solid (4.0 g.) which was recrystallised from nitrobenzene, m.p. 238°. (Found : N, 12.45. $C_{18}H_{11}O_5N_3$ requires N, 12.03 per cent).

(IV). *3-tert.-Butyl-1-nitrophenoxazine* was obtained in the usual way from 4-chloro-3 : 5-dinitro-1-*tert.*-butylbenzene (3.3 g.), *o*-aminophenol (1.5 g.), ethyl alcohol (15 c.c.), 2*N* sodium acetate (*ca.* 8 c.c.) and 2*N*-NaOH (*ca.* 10 c.c.), as a dark brown powder. It was recrystallised from *o*-xylene in shining dark brown needles, m.p. 170°, yield 4.0 g. (Found : N, 10.10. $C_{16}H_{16}O_3N_2$ requires N, 9.85 per cent).

3-Imino-1-phenylphenoxazine (I′).—1-Phenyl-3-nitrophenoxazine (1 g.), suspended in glacial acetic acid (30 c.c.), was reduced at ordinary temperature by shaking in an

atmosphere of hydrogen (60 lbs. pressure) for 12 hours, using Adams' catalyst (60 mg.). The colorless solution obtained immediately turned red on exposure to air. The solution was filtered, concentrated in vacuo to 10 c.c. and made alkaline with dilute NaOH. The crude base, thus separated, was dissolved in benzene and kept over anhydrous sodium sulphate overnight. On passing dry HCl gas through the benzene solution, the imine hydrochloride separated out (1 g.) which was filtered off, washed with dry benzene and dried in vacuum.

Attempts to remove the small amount of water-insoluble material from the hydrochloride failed, and hence, it was converted into the picrate.

The picrate was easily obtained as a red precipitate by adding a saturated aqueous picric acid solution to a filtered aqueous solution (red) of the imine hydrochloride. Recrystallisation from a mixture of saturated aqueous picric acid and ethanol (3 : 4) furnished fine red crystals (3-imino- 1-phenylphenoxazine picrate), m.p. 195°. (Found : N, 14.25. $C_{18}H_{12}ON_2.C_6H_3O_7N_3$ requires N, 13.91 per cent).

1-*Imino*-3-*phenylphenoxazine* (II′).—3-Phenyl-1-nitrophenoxazine (1 g.) was also reduced in the same way, using Adams' catalyst (60 mg.) in the medium of glacial acetic acid (30 c.c.) with 60 lbs. initial pressure of hydrogen. The colorless solution thus obtained turned red on exposure. The base, obtained on making the solution alkaline with caustic soda solution, was converted into the hydrochloride (1 g.) by the same process. The imine hydrochloride was quite soluble in water and alcohol but contained some water-insoluble impurity.

Aqueous solution of the imine hydrochloride afforded on treatment with a saturated aqueous picric acid solution, a reddish brown precipitate of 1-imino-3-phenylphenoxazine picrate. It was also recrystallised from a mixture of alcohol and aqueous picric acid, m.p. 180°. (Found : N, 13.82. $C_{18}H_{12}ON_2.C_6H_3O_7N_3$ requires N, 13.91 per cent).

1 : 4′-*Di-imino*-3-*phenylphenoxazine* (III′).—Reduction of 3-(4′-nitrophenyl)-1 nitrophenoxazine was carried out by the same technique. In this case, however, the reduced solution turned green and ultimately deep blue on exposure. The hydrochloride, obtained from the base, contained water-insoluble material as usual. The aqueous solution of the imine hydrochloride was also blue. On adding saturated aqueous picric acid to it, a deep green precipitate of the picrate was obtained, which was recrystallised from a mixture of alcohol and aqueous picric acid, m.p. 182°. (Found : N, 16.0. $C_{18}H_{12}ON_2$. $C_6H_3O_7N_3$ requires N, 16.31 per cent).

1-*Imino*-3-tert.-*butylphenoxazine* (IV′).—3-*tert.*-Butyl-1-nitrophenoxazine was reduced catalytically by the same procedure, yielding a colorless solution. This solution also turned red on exposure. The base separating, after treatment with dilute NaOH, was converted into its hydrochloride which contained about 33% water-insoluble material. The aqueous extract was therefore concentrated to half the volume before addition of saturated aqueous picric acid. The reddish brown picrate, thus obtained, was recrystallised in the usual way, m.p. 300° (decomp.). (Found: N, 14.84. $C_{16}H_{16}ON_2$. $C_6H_3O_7N_3$ requires N, 14.55 per cent).

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SIGNIFICANCE OF MULTIPLE PATHWAYS IN ADAPTATION. PART I. INHIBITION OF SPORULATION OF *ASPERGILLUS NIGER* AS INDUCED BY EXPOSURE TO TRIPHENYLMETHANE DYES

By S. K. Bose

Normally the spores of a given strain of *A. niger* take nearly 35 hours for sporulation, the period of which is progressively delayed by increased doses of exposure to methyl violet. This delaying effect finally attains a constant value, independent of the duration of exposure. The pattern of inhibition of sporulation, as induced by methyl violet, is the same as by the two other triphenylmethane dyes.

A vital cell process like sporulation may have multiple pathways for adaptation in response to a stimulus.

The phenomenon of adaptation has been accounted for by two major classes of hypotheses- one class involving the assumption that individuals themselves are the primary seat of direct adaptive changes and the other, involving the assumption that individuals of all possible properties do exist in an apparently homogeneous culture. The former operates by actual modification of cells and the latter by selection (Laser, *Biochem. J.*, 1952, **51**, 57; Eddy, *Proc. Roy. Soc.*, 1954, **B142**, 267; Stanier, *Ann. Rev. Microbiol.*, 1951, **5**, 35). The present communication is restricted to a study of the first of the two hypotheses.

The direct adaptive changes of cells, initiated by a given stimulus and very often lost on its withdrawal (as opposed to mutation), are supposed to be due to potentialities or intrinsic virtues rather than newly developed properties of an organism to fight or to adjust itself to a changed environment; these virtues are, as a matter of fact, originally present in the organism in the form of multiple metabolic routes for a given biochemical performance. Instances of multiple pathways for a given biochemical function are not rare. Triple pathways (Lipman, *Nature*, 1936, **138**, 588; Dickens, *ibid.*, p. 1057) of glucose oxidation may be cited as an instance. However, the above assumption to account for adaptation demands that each of the metabolic reactions, particularly those relating to vital cell processes viz., germination, sporulation, respiration etc., must have multiple routes in one and the same organism (Bose, *Science & Culture*, 1955, **21**, 168).

The present work has therefore been undertaken to study whether or not multiple pathways to account for adaptation are involved in the sporulation of a given strain of *A. niger*.

Experimental

Organism and Media.—The organism used in these experiments was a strain of *A. niger* G_3Br. It was maintained on an agar medium consisting of glucose (50.0 g.),

sodium nitrate (2.0 g.), potassium dihydrogen phosphate (1.0 g.), magnesium sulphate (0.5 g.), yeast extract (0.5 g.), malt extract (0.5 g.) and potato extract (hot water extract of 100 g. of potatoes per litre).

The medium used for experimental work, viz., harvesting of spores, determining the period of sporulation etc., was the same as the maintenance medium.

Method of obtaining conidium suspension free from vegetative growth, technique of exposure to dyes, etc. were detailed in an earlier publication (Mazumdar and Bose, *Ann. Biochem. Expt. Med.*, 1955, **15**, 1). A spore suspension was freed from vegetative growth by filtration through wet cotton wool. In exposing these spores they were suspended in a concentration of 10^7 per c.c. in an 1% aqueous solution of triphenylmethane dyes, viz., methyl violet, crystal violet and malachite green.

Method of determining the Period of Sporulation.—The spores freed from vegetative growth were inoculated into a molten agar medium and then 2 to 3 drops of the inoculated medium were uniformly smeared with the help of a loop handle on the surface of a microscopic slide, placed on a wet cotton pad, kept inside a sterile petri dish; and the whole was placed in an incubator at 30°. A series of petri dishes were similarly treated for the purpose. It should be noted here that the number of spores in a smear preparation was adjusted to be very small, otherwise luxuriant growth of mycelial threads would make observation difficult.

After regular intervals microscopic slides, so incubated, were taken out and observed under a microscope using lactophenol as the mounting fluid. In practice, the time-interval between inoculation and formation of the first conidium was taken as the period of sporulation.

The size of spore-head being larger, it was not possible to determine in a given smear preparation the percentage of spores sporulating at different periods of incubation. The time of sporulation of as many as five different spores in any preparation was therefore determined.

The period of sporulation of exposed spores was similarly determined. In practice, treated spores after a given period of exposure were washed several times aseptically till the washing liquid became colorless. It was, however, observed that dyes, not mechanically adhering to the surface of spores but physically adsorbed on them, could not be removed. The spores, thus washed free of dyes, were treated in the same way as referred to above for determining the period of sporulation.

Period of Sporulation at Different Levels of Exposure to Methyl Violet.—The sporulating period is normally different with different spores (Table IA). It may vary from 32.5 to 38.0 hours. This difference in absence of any treatment may be regarded as individual variation. Previous exposure to methyl violet tends to inhibit sporulation so much that it may now take more time than what is normally required. To ascertain the significance of this observed inhibition, the data were subjected to 'F' test by statistical methods (Table IB).

The high value of 'F', as shown in Table IB, clearly indicates that all the treatments are significant, whereas the data due to replications are not significantly different. Comparing the difference between the means for the blank and treatments with the

critical difference at 5% (2.79) and 1% (3.85) levels, it is found that all exposures are significant at both the levels ; exposure for 3 days is not significantly effective when compared with 1 day's exposure. Exposures for 3, 5 and 7 days have the highest inhibiting effect, but amongst themselves they do not vary significantly. It can therefore be concluded from statistical analysis that the maximum inhibiting effect is observed up to 5 days' exposure and beyond this, the effect is not significant.

TABLE IA

Effect of exposure to methyl violet on the period of sporulation.

Individual spore.	Period of sporulation after exposure for 0 day.	1 day.	3 days.	5 days.	7 days.
1	33.0 hrs.	41.0 hrs.	46.0 hrs.	44.5 hrs.	47.0 hrs.
2	37.0	39.0	44.0	42.0	43.5
3	36.0	43.5	43.5	43.0	46.0
4	33.0	42 5	42.5	47.0	45.0
5	36.0	39.0	41.5	46.0	41.0
Mean	35.0	41.0	43.5	44.5	44.5

TABLE IB

Analysis of variance (methyl violet).

Sources of error.	D. F.	S. S.	M. S.	F.	Significance.
Replications	4	11.50	2.875	...	
Treatments	4	321.50	80.375	18.50	Significant
Error	16	69.50	4.344	...	
Total	24	402 50			

Pattern of Inhibition induced in Sporulation by Triphenylmethane Dyes.—The effect of exposure to crystal violet and malachite green on sporulation was studied (Tables IIA and IIIA) and the data were subjected to statistical analysis (Tables IIB and IIIB). It appears that crystal violet and malchite green also exert delaying action on sporulation. The statistical analysis of the data clearly points out that all the treatments are significant not only with respect to control but also amongst themselves except after 5 days' exposure, beyond which almost a constant value is attained. Thus, the pattern of inhibition induced is the same as in the case of methyl violet.

TABLE IIA

Effect of exposure to crystal violet on the period of sporulation.

Individual spore.	Sporulating period after exposure for 0 day.	1 day.	3 days.	5 days.	7 days.	9 days.
1	32.5 hrs.	42.0 hrs.	43.0 hrs.	47.0 hrs.	45.0 hrs.	47.5 hrs.
2	37.5	44.0	41 0	42.0	43.0	44.0
3	36.0	39.0	46.5	44 5	48.5	42.0
4	34.0	45.0	46.0	43.0	46.0	45.5
5	35.0	40.0	41.0	46.0	42.5	46.0
Mean	35.0	42.0	43.5	44.5	45.0	45.0

TABLE IIIB

Analysis of variance (crystal violet).

Sources of error.	D. F.	S. S.	M. S.	F.	Significance
Replications	4	9.83	2.46	...	
Treatments	5	370.00	74.00	12.65	Significant
Error	20	116.67	5.83	...	
Total	29	496.50	...		

TABLE IIIA

Effect of malachite green on the period of sporulation.

Individual spore.	Sporulating period after exposure for 0 day.	1 day.	3 days.	5 days.	7 days.
1	34.5 hrs	47.0 hrs.	43.5 hrs.	50.5 hrs.	45.0 hrs.
2	32.5	46.5	49.0	49.0	48.0
3	38.0	42.0	44.5	48.0	45.5
4	34.0	44.0	47.5	47.0	50.0
5	36.0	43.0	48.0	45.5	50.5
Mean	35.0	44.5	46.5	48.0	48.0

TABLE IIIB

Analysis of variance (malachite green).

Sources of error.	D. F.	S. S.	M. S.	F.	Significance.
Replications	4	5.3	1.3	...	
Treatments	4	593.5	148.3	26.9	Significant
Error	16	88.7	5.5	...	
Total	25	687.5	...		

CONCLUSION

Normally the spores of the given strain of *A. niger* take 35 hours to sporulation. Data obtained show that previous exposure to methyl violet delays normal sporulation. This progressively increased delay, which attains a constant value, may indicate that more than one biochemical paths are involved in sporulation and that at least one of these paths is probably sensitive to the action of the dye. Inhibition studies, as conducted with the two other triphenylmethane dyes, also indicate the same pattern of inhibition, which implies that more than one biochemical paths may be involved in the process.

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RHODANINE-N-SALICYLIC ACID AND ITS USE IN THE ESTIMATION OF THORIUM

By M. K. Rout

Rhodanine-N-salicylic acid has been used for the estimation of thorium. On the basis of the weight of the complex obtained, a probable structure has been proposed for the thorium complex. Additional support in favour of the proposed structure has been provided by ignition of a definite weight of the complex to ThO_2.

Many organic compounds like fumaric acid, *m*-nitrobenzoic acid, phenylarsonic acid, sodium anthranilate and sebacic acid etc. have been used as precipitating reagents for thorium (Metzger, *J. Amer. Chem. Soc.*, 1902, **24**, 901 ; Neish, *Chem. News*, 1904, **90**, 196; Riss and Foggs, *J. Amer. Chem. Soc.*, 1926, **48**, 893 ; Goto, *J. Chem. Soc., Japan*, 1934, **55**, 1156 ; James and Smith, *J. Amer. Chem. Soc.*, 1912, **34**, 281).

Some of these reagents have also been successfully used for separation of thorium from rare earths. Raghava Rao and his co-workers have used chloro- and aminobenzoic acids, phenoxyacetic acids and trimethylgallic acid etc. for the quantitative estimation and separation of thorium (this *Journal*, 1950, **27**, 457, 459, 81). Datta and Banerjee have also successfully employed 2 : 4-dichlorophenoxyacetic acid and 5-iodoanthranilic acid for the same purpose (*ibid.*, 1954, **31**, 397, 229, 773, 779).

In course of our investigations on thiohydantoins, thiazolidones and rhodanines, we studied the possibility of their use as precipitating agents for thorium. In preliminary screening experiments, all these reagents, except rhodanines, failed to precipitate thorium completely and quantitatively.

Experimental

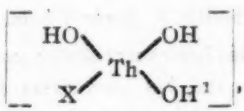
Rhodanine-N-salicylic Acid.—Dithiocarbamate of *p*-aminosalicylic acid was prepared by taking a mixture of *p*-aminosalicylic acid (13.5 g.) and KOH (11.2 g.) in water (50 c.c.) in a round bottomed flask fitted with a mechanical stirrer and surrounded by an ice-bath. The temperature was not allowed to exceed 10°. CS_2 (7.5 c.c.) was slowly run into the flask from a separating funnel. Stirring was continued until the CS_2 layer disappeared, indicating completion of the reaction.

Potassium monochloroacetate was prepared by mixing a solution of KOH (5.6 g.) in water with a solution of monochloroacetic acid (9.4 g.) in water. Sodium carbonate was added till the solution was neutral to litmus.

To the potassium monochloroacetate solution, thus prepared, the dithiocarbamate was added slowly with stirring and good cooling. The stirring was continued for some time more. Then the mixture was added under stirring to HCl (conc., 15-18 c.c.), previously heated to 90°, when a yellow precipitate was obtained. It was stirred for one hour more and then allowed to stand in an ice-bath for another hour. The rhodanine was filtered and washed with water and recrystallised from alcohol, m.p. 117°, yield 75%. (Found : N, 5.34. $C_{10}H_7O_4NS_2$ requires N, 5.20 per cent).

Estimation of Thorium.—A stock solution of thorium nitrate was prepared and the thorium content was determined by a standard method using *m*-nitrobenzoic acid.

Thorium nitrate solution (25 c.c.) from the stock solution was taken in a beaker and was made just neutral to Congo red by adding dilute ammonia. An excess of an 1% solution of the reagent in alcohol was added. The necessary amount of the excess reagent was established by a series of experiments in which the amount of reagent was varied from 1.7 to 10-fold excess. The data indicated that a four-fold or a slightly greater excess was adequate. A precipitate appeared immediately. The complex was then warmed on a water-bath for 15 minutes and kept overnight. The complex was filtered in a G_3 crucible, washed with hot water and dried at 110°-115°. The weights of the complex formed in different sets of experiments from the same volume of thorium nitrate solution were found to be nearly the same (Table I). On the basis of the weights, the following formula for the complex is proposed.



$2H_2O$.

[X = residue of 2-mercaptothiazolidone-N-salicylic acid].

TABLE I

Thorium taken (as nitrate in g.)	0.0632	0.0632	0.1264	0.1264	0.1896	0.1896
Weight of complex (g.)	0.1585	0.1625	0.3215	0.3226	0.4776	0.4826
% Thorium (found)	39.87	38.90	39.31	39.18	39.71	39.30
% Thorium (calc. on the basis of the proposed structure)	39.53					

Thorium has also been estimated from the weight of ThO_2 obtained by ignition of the complex formed with the organic reagent. As will appear from Table II, the results compare well with the data obtained by using standard *m*-nitrobenzoic acid method.

TABLE II

Reagent.	ThO_2 found in g.				
m-Nitrobenzoic acid	0.0948	0.0956	0.0952	0.1906	0.2842
Rhodanine-N-salicylic acid	0.0952	0.0955	0.951	0.1895	0.2851

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FORMATION OF COMPLEX COMPOUNDS BETWEEN CADMIUM HALIDES AND ALKALI HALIDES. PART I. SYSTEM $CdCl_2$—NH_4Cl—H_2O

By K. G. Kaimal and A. K. Bhattacharya

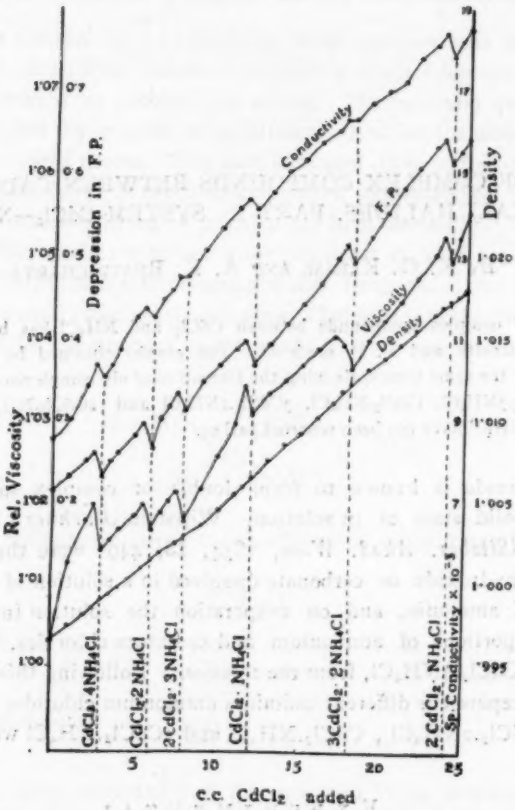
The formation of complex compounds between $CdCl_2$ and NH_4Cl has been studied by the conductivity, density, viscosity and F. P. methods. The graphs obtained by all the methods show six breaks at exactly the same points, showing the formation of six complexes, namely, $CdCl_2.4NH_4Cl$, $CdCl_2.2NH_4Cl$, $2CdCl_2.3NH_4Cl$, $CdCl_2.NH_4Cl$, $3CdCl_2.2NH_4Cl$ and $2CdCl_2.NH_4Cl$, of which $2CdCl_2.3NH_4Cl$ and $3CdCl_2.2NH_4Cl$ have not been reported earlier.

Cadmium chloride is known to form double or complex salts with ammonium chloride in the solid state or in solution. Wittstein (*Buchner's Report*, 1837, **57**, 32) and Von Hauer (*Sitzber. Akad. Wien*, 1854, **13**, 449) were the first to observe that cadmium oxide, hydroxide or carbonate dissolved in a solution of ammonium chloride with evolution of ammonia, and on evaporation the solution furnished crystals with very variable proportions of ammonium and cadmium chlorides. Von Hauer isolated the hexachloride, $CdCl_2.4NH_4Cl$, from the solution. Following this observation various workers tried to prepare the different cadmium ammonium chlorides and the compounds $CdCl_2.4NH_4Cl$, $CdCl_2.2NH_4Cl$, $CdCl_2.NH_4Cl$ and $2CdCl_2.NH_4Cl$ were reported.

Experimental

The substances used were of A. R. quality. Stock solutions of cadmium chloride and ammonium chloride were prepared by dissolving the calculated amounts of the respective salts in conductivity water to form $M/4$ solutions. The method of Nayer and Pande (*Proc. Ind. Acad. Sci.*, 1947, **27A**, 286) of keeping the concentration of one of the constituents constant and varying the other systematically was adopted to prepare the subsequent solutions. In this case the concentration of ammonium chloride was kept constant and varying amounts of cadmium chloride were added. Every time the solution was made up to 50 c c. in a standard flask with conductivity water. In this way 35 mixed solutions were prepared and subjected to study by the conductivity, density and freezing point measurements. The results are shown graphically. From the graph it can be seen that six definite breaks are obtained by all the three methods at exactly the same points, showing the existence in solution of the compounds $CdCl_2.4NH_4Cl$, $CdCl_2.2NH_4Cl$, $2CdCl_2.3NH_4Cl$, $CdCl_2.NH_4Cl$, $3CdCl_2.2NH_4Cl$ and $2CdCl_2.NH_4Cl$. Of these, only those with ratios 1 : 4, 1 : 2, 1 : 1 and 2 : 1 have been reported earlier. The other two appear to be new compounds.

FIG. 1



Additional work as proof for the existence of these compounds is being done by E.M.F. measurements and absorption spectra studies. Efforts are also being made to isolate the compounds, if possible.

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SYNTHESIS OF SOME DIARYLSULPHONES

By A. B. Sen and A. K. Roy

Several diarylsulphones have been prepared by the application of the Fries rearrangement and the Friedel-Crafts reaction, with a view to testing them for their antibacterial activity.

The importance of hydroxydiarylsulphones as useful antiseptics (cf. Amin, Desai, Parekh and Venkataraman, *J. Sci. Ind. Res.*, 1954, **13B**, 181) has encouraged the authors to undertake the synthesis of several hydroxy- and methoxy-diarylsulphones.

Much work has been done in this series by Rittler (D.R.P. 532403/1930), Simons, Archer and Rendall (*J. Amer. Chem. Soc.*, 1940, **62**, 485), Aleykutty and Baliah (this *Journal*, 1954, **32**, 513) and Amin *et al.* (*loc. cit.*) who obtained these sulphones by the Fries migration of the corresponding sulphonic esters of the phenol as well as by the Friedel and Crafts reaction between the sulphonyl chlorides and the aromatic hydrocarbons (cf. Beckerts and Otto, *Ber.*, 1878, **11**, 2066; Witt and Uermenye, *Ber.*, 1913, **46**, 306; Rittler, D. R. P. 555409/1931).

In the present investigation the authors have synthesised a few sulphones by the Fries rearrangement of the toluenesulphonic esters of *ortho*- and *para*- halogenated and alkyl phenols. The esters were obtained by the addition of 10% aqueous solution of caustic soda to a solution of the phenol and the sulphonyl chloride in acetone.

It was, however, observed that the rearrangement was successfully effected only in two cases, viz., (1) 6 chloro-3-methylphenyl-*p*-toluenesulphonate and (2) 2:4-dichlorophenyl-*p*-toluenesulphonate, and completely failed in other esters even under varying conditions (*i. e.* in nitrobenzene solution even at higher temperature). The product obtained by the Fries rearrangement of the ester (1), when coupled with 2:4-dichlorobenzenediazonium chloride, furnished an orange dye which could not be methylated by dimethyl sulphate in presence of acetone and anhydrous potassium carbonate. The dye therefore has the chelated *o*-hydroxy-azo structure, and hence, it is beyond doubt that the *p*-toluenesulphonyl group migrates to the position *para* to the hydroxy group in this case. The ester (2) afforded the *ortho*-substituted sulphone, the *para* position being occupied.

The sulphones, which could not be prepared by the Fries rearrangement of their corresponding sulphonic esters, were obtained by the Friedel and Crafts reaction.

Four sulphones (No. 1, 2, 3 & 4, Table III) were prepared by the action of *p*-toluenesulphonyl chloride on the methyl ethers of the corresponding phenols in carbon disulphide in the presence of anhydrous aluminium chloride. The substitution in No. 1, 2 and 3 was in the *ortho* position to the methoxy group, as the *para* positions in these compounds were not free. The substitution in the compound No. 4 was assigned in the *para*, position as one of the *ortho* positions to the methoxy group was not free and the other one was hindered.

The rest of the sulphones (No. 5-8, Table III) were obtained by the condensation of ethylbenzene and *p-sec.*- amylbenzene with *p*-chlorobenzenesulphonyl chloride and *p*-methoxybenzenesulphonyl chloride in the same manner. In all the above cases, *para*-substituted sulphones were obtained.

EXPERIMENTAL

Phenolic Esters of p-*Toluenesulphonyl Chloride.*—The esters were prepared by adding an aqueous 10% caustic soda solution dropwise with constant stirring to a solution of the phenol (1 mole) and *p*-toluenesulphonyl chloride (1.1 mole) in acetone until the mixture was slightly alkaline. After this the mixture was stirred for half an hour, cooled and filtered. The crystals, thus obtained, were recrystallised from alcohol. The melting point, yield and analysis of the esters obtained are summarised in Table I.

TABLE I

[T denotes *p*-toluenesulphonate].

No.	Ester.	M.P.	Yield.	% Sulphur. Found.	Calc
1.	4-*tert.*-Butylphenyl-T	111°	62%	10.36	10.52
2.	4-*tert.*-Amylphenyl-T	51°	65	9.92	10.06
3.	6-Chloro-3-methylphenyl-T	99-100°	63	10.47	10.80
4.	2-Diphenyl-T	65°	60	9.68	9.87
5.	4-Diphenyl-T	175-76°	68	9.71	9.87
6.	2-Chloro-4-*tert.*-butylphenyl-T	90-91°	72	9.23	9.46

Fries Rearrangement of the Esters.—The Fries migration of the esters was carried out in the following way. The ester (1 *M*) was dissolved in CS_2 (30 c. c.) and after addition of $AlCl_3$ (anhyd., 1.5 *M*) was refluxed over a steam-bath for an hour. CS_2 was then distilled off and the mixture was heated in an oil-bath at 120° for an hour. After cooling, the solid was decomposed with ice-cold HCl. The crude solid was filtered off and crystallised from dilute alcohol.

It was found that only one of the above esters, viz., No. 3 and 2 : 4-dichlorophenyl-*p*-toluenesulphonate, underwent rearrangement, while in the other five cases the esters were recovered unchanged. Even when the Fries migration was carried out in nitrobenzene solution at higher temperatures (120°-140°), these five esters remained unchanged as such, only the following two sulphones were obtained (Table II).

TABLE II

No.	Sulphones.	M.P.	Yield.	% Sulphur. Found.	Calc.
1.	4-Hydroxy-5-chloro-2-methylphenyl *p*-tolyl-	276°	40%	10.60	10.80
2.	2-Hydroxy-3 : 5-dichlorophenyl-*p*-tolyl-	152°	50	9.80	10.16

2 : 4-*Dichlorobenzene-azo-2'-hydroxy-3'-chloro-6'-methylphenyl-5''*-p-*tolylsulphone.*—2 : 4-Dichloroaniline was diazotised in the usual way and then coupled in the cold with a solution of 4-hydroxy-5-chloro-2-methylphenyl-*p*-tolylsulphone in caustic soda. On

acidification a solid was obtained which was filtered and crystallised from alcohol, m.p. 123°. (Found : N, 5.69. $C_{20}H_{13}O_3N_2Cl_3S$ requires N, 5.96 per cent).

The eight sulphones in Table III were prepared by the Friedel-Crafts reaction, using CS_2 as the solvent.

TABLE III

No.	Phenol ether & hydrocarbon.	Sulphone.	M.P.	Yield.	% Sulphur. Found.	Calc.
1.	*p-tert.*-Butylphenyl-methyl ether	2-Methoxy-5-*tert.*-butyl-phenyl-*p*-tolyl-	98°	45%	9.92	10.06
2.	*p*-Methoxydiphenyl	2-Metboxy-5-phenyl-benzene-*p*-tolyl-	172°	60	9.06	9.45
3.	*p-tert.*-Amylphenyl-methyl ether.	2-Methoxy-5-*tert.*-amylphenyl-*p*-tolyl-	125°	52	9.22	9 63
4.	3-Methyl-6-*tert.*-butyl-phenylmethyl ether	4-Methoxy-5-*tert.*-butyl-2-methylphenyl-*p*-tolyl-	100°/4mm. (B.P.)	42	9.32	9.63
5.	Ethylbenzene	4-Ethylphenyl-*p*-methoxyphenyl-	98°	55	11.26	11.23
6.	*sec.*-Amylbenzene	4-*sec.*-Amylphenyl-*p*-methoxyphenyl-	77°	58	9.75	10.00
7.	Ethylbenzene	4-Ethylphenyl-*p*-chloro-phenyl-	120°	48	9.90	10.03
8.	*sec.*-Amylbenzene	4-*sec.*-Amylphenyl-*p*-chlorophenyl-	148°	53	11.10	11.40

Friedel-Crafts Reaction between the Methyl Ethers of the Phenol and p-*Toluenesulphonyl Chloride*—The sulphones (No. 1-4, Table III) were prepared by dissolving the corresponding phenol ether (1 *M*) and the *p*-toluenesulphonyl chloride (1.1*M*) in 30 c.c. of CS_2 and then adding $AlCl_3$ (anhyd., 1.5 *M*) gradually. The reaction started immediately with the evolution of HCl fumes. After the addition of $AlCl_3$, the mixture was refluxed for one hour, CS_2 distilled off and the aluminium complex decomposed with ice and HCl. The solid obtained after filtration was recrystallised from alcohol and water.

Friedel-Crafts Reaction between the Aromatic Hydrocarbons and p-*Methoxybenzenesulphonyl Chloride.*—The sulphones (No. 5 & 6, Table III) were obtained by the action of *p*-methoxybenzenesulphonyl chloride (1.1*M*) on ethylbenzene (1 *M*) and *p-sec.*-amylbenzene (1 *M*) in CS_2 (30 c.c.) in presence of $AlCl_3$ (anhyd., 1.5 *M*) by the same procedure. The *p*-methoxybenzenesulphonyl chloride was obtained by the method used by Morgan and Cretchen (*J. Amer. Chem. Soc.*, 1948, **70**, 375).

Friedel-Crafts Reaction between the Aromatic Hydorcarbons and p-*Chlorobenzenesulphonyl Chloride.*—The sulphones (No. 7 & 8, Table III) were obtained by the same procedure as above except that *p*-chlorobenzenesulphonyl chloride was used in place of *p*-methoxybenzenesulphonyl chloride. The former was obtained by the method used by Ullmann and Korselt (*Ber.*, 1907, **40**, 742).

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2-*p*-AMINOPHENYLIMINO-4-THIAZOLIDONE AND SOME OF ITS DERIVATIVES

By M. K. Rout

2 *p*-Aminophenylimino-4-thiazolidone and its arylidene derivatives have been prepared by reduction with iron and acetic acid of the corresponding 2-*p*-nitrophenylimino-4-thiazolidone and its arylidene compounds. The compounds thus prepared have been mercurated and also brominated. The position of acetoxymercuri group, introduced on mercuration, has been determined. 2-*p*-Aminophenylimino-4-thiazolidone does not undergo nuclear substitution on bromination. The fungicidal properties of both the brominated and mercurated compounds have been evaluated.

In course of our investigations, we have developed a new and very convenient route to the synthesis of thiazolidone compounds (Rout and Mahapatra, *J. Amer. Chem. Soc.*, 1955, **77**, 2427). The method devised by us (illustrated here by the preparation of 2-*p*-nitrophenylimino-4-thiazolidone) consists of heating aryl thiocarbamides with chloroacetic acid in absolute alcohol in presence of anhydrous sodium acetate, and has certain advantages over that of Desai, Hunter and Kopper (*Rec. trav. chim.*, 1935, **54**, 118) in that the procedure adopted by us is more rapid and does not involve the isolation of the intermediate substituted formamidine-thiol-acetic acid. It has also been shown that some of these thiazolidone compounds can be successfully used in analytical procedures for estimation of Ag, Hg and Cu (Das and Rout, *J. Sci. Ind. Res.*, 1955, **14B**, 16). In course of preparing different series of new thiazolidone derivatives and exploring new possibilities for their applications, it appeared of interest to prepare 2-*p*-aminophenylimino-4-thiazolidone, since the amino group would provide easy routes to the introduction of several therapeutically active groups like arsenic, sulphonamide, thiourea, thiosemicarbazide, etc. This compound could not obviously be prepared by the reaction of *p*-aminophenylthiourea with chloroacetic acid because of the presence of the reactive $-NH_2$ group which would condense with ease with chloroacetic acid. The only convenient route which suggested itself was by reduction of the corresponding 2-*p*-nitrophenylimino-4-thiazolidone which could be easily obtained by reaction of 2-*p*-nitrophenylthiourea with chloroacetic acid. The reduction was effected by iron filings and glacial acetic acid in alcohol medium.

To prepare the corresponding arylidene derivative, the conventional method could not be applied. The potential carbonyl group would not only combine with the $-CH_2$ group of the thiazolidone nucleus but also with the NH_2 -group of the substituted arylimino group. The method which was adopted here involved the reduction of the corresponding arylidene derivatives of 2-*p*-nitrophenylimino-4-thiazolidone, by iron filings and acetic acid, exactly in the same manner as in case of the parent compound, 2-*p*-nitrophenylimino-4-thiazolidone.

The preparations of 2-*p*-aminophenylimino-4-thiazolidone and its arylidene derivatives are illustrated in the Experimental. The preparations of the intermediate

products, 2-*p*-nitrophenylimino-4-thiazolidone and its arylidene derivatives, are also described along with them.

The compound, 2-*p*-aminophenylimino-4-thiazolidone (in form of its acetyl derivative) has also been brominated. In the bromination of diaryl-ψ-thiohydantoins, it has been reported that the keto enol system is not affected and polybromide-addition compounds of highly complex nature are formed (Farooq and Hunter, this *Journal*, 1932, **9**, 545; Choudhury, Desai, Hunter and Solangi, *Rec. trav. chim.*, 1933, **52**, 853). The thiazolidone compounds, studied here, however, do not possess the second aryl nucleus which is substituted by bromine in case of diaryl-ψ-thiohydantoin. A study of the behaviour of this compound towards bromine, likely to prove of interest, was therefore undertaken. On treatment of the thiazolidone compound with bromine in chloroform under ice cooling, a vermillion-coloured bromine-addition compound was formed. Attempts to determine the nature of this complex revealed that all the bromine was in a labile state as it was completely removed by sulphurous acid and also HgO, regenerating the original compound. These observations completely rule out the following possibilities: (*i*) addition of bromine to the double bond of 2-phenylimino grouping in the original thiazolidone, (*ii*) the formation of a sulphonium bromine in which case, on treatment with HgO, a sulphoxide and not the original thiazolidone would have been formed; (*iii*) nuclear substitution of the aryl nucleus. Hence, the bromine-addition compound cannot be of the nature of hydroperbromide and may be dibromide of the type formed between benzthiazole and bromine in an inert solvent (Hunter, *J. Chem. Soc.*, 1950, 125; Dyson, *et al.*, this *Journal*, 1931, **8**, 147).

Since brominated thiazolidone (with bromine attached to the ring) could not be obtained in this manner, bromination of arylidene derivatives of thiazolidones was undertaken. Bromine reacted with the vinyl group, yielding stable dibromides and one of the two bromine atoms was attached to the thiazolidone ring. Only four such compounds have been brominated. The fungicidal activities of these compounds have also been determined.

2-*p*-Aminophenyliminothiazolidone and three of its arylidene derivatives have also been mercurated. The acetoxymercuri group enters the arylimino group. Other possibilities have been ruled out. The compound is not decomposed by alkali, thus indicating that Hg does not replace the H-atom of the -NH group in position-3. The acetoxymercuri group does not substitute the $-CH_2$ group as both the thiazolidone and its arylidene products can be mercurated under identical conditions.

EXPERIMENTAL

2-p-*Aminophenylimino-4-thiazolidone* was prepared by reduction of 2-*p*-nitrophenylimino-4-thiazolidone, which in turn was prepared as follows:

A mixture of *p*-nitrophenylthiourea (6 g.), monochloroacetic acid (3 g.), anhydrous sodium acetate (3 g.) and absolute alcohol (25 c.c.) was refluxed for 2 hours. The reaction mixture was cooled and then poured into cold water. The

yellow precipitate formed was allowed to settle and filtered. It was washed several times with hot water, recrystallised from alcohol and dried, m.p. 225°, yield 70%. (Found : S, 13.72. $C_9H_7O_3N_3S$ requires S, 13.5 per cent).

A mixture of 2-*p*-nitrophenylimino-4-thiazolidone (5 g.), alcohol (36 c.c.), iron filings (20 g.), glacial acetic acid (10 c.c.) and water (20 c.c.) was refluxed with stirring for one hour. Glacial acetic acid (1 c.c.) was again added to the mixture and stirring was continued for two hours more. The mixture was basified with sodium carbonate and filtered while hot. Alcohol was removed by distillation. The aqueous mixture was further evaporated till the bulk was considerably reduced. It was cooled and on addition of water 2-*p*-aminophenylimino-4-thiazolidone separated out. It was filtered and the residue was washed well with cold water and recrystallised from alcohol, m.p. 206°, yield 50%. (Found : S, 15.29. $C_9H_9ON_3S$ requires S, 15.46 per cent).

5-*Benzylidene*-2-p-*aminophenylimino*-4-*thiazolidone* was prepared by reduction of 5-benzylidene-2-*p*-nitrophenylimino-4-thiazolidone, which in turn was prepared as follows :

A mixture of benzaldehyde (1 g.) and 2-*p*-nitrophenylimino-4-thiazolidone (1.5 g.) was refluxed in glacial acetic acid (about 25 c.c.) in presence of anhydrous sodium acetate (about 1.5 g.) on an asbestos wiregauze for 2 hours. The clear solution after being cooled was poured into water yielding a dirty yellow precipitate. After stirring thoroughly and allowing the precipitate to stand overnight, the solution was filtered off, the precipitate washed well in water and it was recrystallised from alcohol, m.p. 311°, yield 75%. (Found : S, 10.13. $C_{16}H_{11}O_3N_3S$ requires S, 9.85 per cent).

5-Benzylidene-2-*p*-nitrophenylimino-4-thiazolidone was reduced by iron filings and glacial acetic acid in presence of alcohol in the manner already described, m.p. above 320°, yield 75%. (Found : S, 11.10. $C_{16}H_{13}ON_3S$ requires S, 10.84 per cent).

TABLE I

5-Arylidene-2-p-nitrophenylimino-4-thiazolidones.

Comp. No.	Aldehydes providing the arylidene group.	M.P.	Yield.	% Sulphur. Found.	Calc.
1	Benzaldehyde	311°	75%	10.13	9.80
2	*o*-Hydroxybenzaldehyde	252°	80	10.89	10 47
3	*p*-Hydroxybenzaldehyde	>300°	70	10.03	9.37
4	*o*-Nitrobenzaldehyde	264°	60	8.84	8 65
5	*m*-Nitrobenzaldehyde	247°	70	9.05	8.65
6	*p*-Nitrobenzaldehyde	301°	70	9.16	8.65
7	Anisaldehyde	302°	74	9 45	9.90
8	Cinnamaldehyde	265°	75	9.62	9.10
9	Vanillin	256°	80	10.20	9.80

TABLE II

5-Arylidene-2-p-aminophenylimino-4-thiazolidones.

Comp. No.	Aldehydes providing the arylidene group.	M.P.	Yield.	% Sulphur. Found.	Calc.
10	Benzaldehyde	>320°	75%	11.29	10.84
11	*o*-Hydroxybenzaldehyde	180°	65	10.40	10.28
12	*p*-Hydroxybenzaldehyde	>300°	60	10 30	10.28
13	*o*-Nitrobenzaldehyde	290°(d)	60	9.81	9.40
14	*m*-Nitrobenzaldehyde	>300°	65	9.56	9.60
15	*p*-Nitrobenzaldehyde	Do	70	9.91	9.40
16	Anisaldehyde	280°(d)	50	10.10	9.84
17	Cinnamaldehyde	167°	60	9.50	9 90
18	Vanillin	255°	70	9.81	9.80

Bromination of 2-p-*Acetamidophenylimino-4-thiazolidone.*—A solution of 2-*p*-acetamidophenylimino-4-thiazolidone (1 g.) in chloroform (15 c.c.) was treated with bromine (1 c.c. in 2 c.c. of chloroform) and the mixture was kept in ice for 1 hour. As no crystallisation took place, the solution was concentrated under reduced pressure at laboratory temperature, when a vermillion-coloured bromine-addition compound separated. It was collected on a glass-sintered crucible and dried in vacuum over potassium hydroxide, paraffin wax and anhydrous calcium chloride. An orange product was obtained, m.p. 195°.

All the bromine in this compound was in a labile state. The percentage of labile bromine, before treatment with sulphurous acid, was estimated by dissolving the bromine-addition compound in chloroform to which a drop or two of acetic acid had been added and then adding a strong solution of potassium iodide. The iodine liberated on shaking the mixture was titrated with $N/20$ sodium thiosulphate solution. Analysis indicated the presence of two bromine atoms. (Found: Labile Br, 38.48. $C_{11}H_{11}O_2N_3Br_2S$, requires Br, 39.1 per cent).

5-Bromo-5-phenylbromomethyl-2-p-acetamidophenylimino 4-thiazolidone.—A solution of 5-benzylidene-2-*p*-acetamidophenylimino-4-thiazolidone (1 g.) in chloroform (40 c.c.) was cooled to about 0° and then treated with bromine (2 c.c.) in chloroform (8 to 10 c.c.) and the mixture was kept in ice for 1 hour. On concentrating the solution under reduced pressure, a deep red product was obtained which on treatment with sulphurous acid and subsequent basification with ammonia furnished the dibromide of the starting material, m.p. 205°, yield 80%. (Found: Br, 31.96; S, 6.25. $C_{18}H_{15}O_2N_3Br_2S$ requires Br, 32.19; S, 6.44 per cent).

TABLE III

5-Bromo-5-arylbromomethyl-2'-(p-acetamidophenylimino)-4-thiazolidone.

Aldehydes.	M.P.	% Bromine. Found.	Calc	% Sulphur. Found.	Calc.
p-Nitrobenzaldehyde	225°	29.35	29.52	5.70	5.,0
Anisaldehyde	230°	30.12	30.36	5.92	6.07
p-Dimethylaminobenzaldehyde	190°	29.55	29.63	5.68	5.93

2-(o-*Acetoxymercuri*-p-*aminophenylimino*)-4-*thiazolidone*.—A solution of mercuric acetate (2 g.) in 30 to 40 c.c. of water, acidified with 3 to 4 drops of glacial acetic acid, was treated with an alcohol-dilute acetic acid solution of 2-*p*-aminophenylimino-4-thiazolidone (1 g.), and the mixture was stirred vigorously for 10 to 15 minutes, when a precipitate appeared. The reaction mixture was allowed to stand overnight with occasional stirring and then filtered. The precipitate was washed with hot water 3 to 4 times and then with very dilute acetic acid. Finally it was washed with alcohol, m.p. 207°, yield 75%. (Found: S, 6.56; Hg, 42.85. $C_{11}H_{11}O_2N_3SHg$ requires S, 6.88; Hg, 43.01 per cent).

5-*Benzylidene*-2-(o-*acetoxymercuri*-p-*aminophenylimino*)-4-*thiazolidone*.—An alcohol-dilute acetic acid solution of 5-benzylidene-2-(*o*-acetoxymercuri-*p*-aminophenylimino)-4-thiazolidone (1.3 g.) was mixed with vigorous stirring with an aqueous solution of mercuric acetate (3 g.). The reaction mixture was refluxed on a water-bath for about half an hour and then vigorously stirred again for 20 minutes and kept overnight and then filtered. It was purified as the preceding compound, m.p. 205°, yield 75%. (Found: Hg, 35.95. $C_{18}H_{15}O_2N_3SHg$ requires Hg, 36.2 per cent).

TABLE IV

5-*Arylidene*-2-(o-*acetoxymercuri*-p-*aminophenylimino*)-4-*thiazolidone*.

Aldehydes.	M.P.	Yield.	% Mercury. Found.	Calc.
p-Nitrobenzaldehyde	205°	75%	33.12	33.44
Cinnamaldehyde	230°	80	34.21	34.54
Anisaldehyde	235°	75	34.41	34.30

Fungicidal activity was assayed with the test fungus as reported by Rout and Pujari (*J. Sci. Ind. Res.*, 1955, **14B**, 13). The mercurated compounds were very effective, completely inhibiting spore germination even at a dilution of 5 to 6 p.p.m. The dibromide compounds were active nearly to the same extent.

The authors' thanks are due to Sri A.K. Nayak, M.Sc. for occasional assistance.

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A NOTE ON THE EFFECT OF CONCENTRATION OF HYDROCHLORIC ACID ON THE DECOMPOSITION OF MUREXIDE

By N. A. Ramaiah, S. L. Gupta and Vishnu

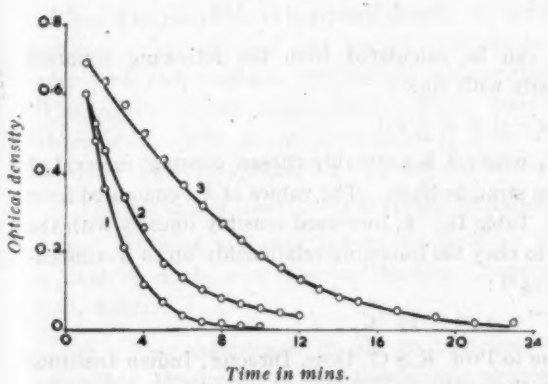
It is known (Davidson and Epstein, *J. Org., Chem.* 1936, **1**, 305) that murexide undergoes decomposition in acidic solutions to furnish uramil and alloxan. No data exist in the literature on the kinetics of this reaction which appears primarily to be an acid hydrolysis. During a series of experiments undertaken in this laboratory to investigate the calcium content in sugarcane juices with the help of murexide, specially using its characteristic absorption spectra, the rate of decomposition of murexide in acid solutions was examined. The present communication reports the effect of the concentration of a strong acid like HCl on the kinetics of the above reaction.

Murexide of B.D.H. quality was used ; this was purified by the method of Davidson (*J. Amer. Chem. Soc.*, 1936, **58**, 1821) yielding 99-100% purity (cf. Moser and Williams, *Anal. Chem.*, 1954, **26**, 1167). Hydrochloric acid of B.D.H.- Analar quality was used. Absorption spectra of murexide were recorded with Unicam 350 D.G. Spectrophotometer, using 10 mm. cells.

Murexide exhibits characteristic absorption maximum at $\lambda = 530$ mμ. The optical density at this wave-length increased sensibly linearly with the concentration of murexide, providing a value of 1.04×10^4 mole/litre^{-1} cm^{-1} for the Beer's constant.

The data in Fig. 1 show the variation with time of the optical density of murexide of a fixed concentration (0.10 m*M*) at the optimum wave-length $\lambda = 530$ mμ ; here, curves 1, 2 and 3 refer to different concentrations of HCl, viz., 10, 6.25 and 2.5m*M* respectively. These data were obtained as follows :

Fig. 1



(Conc of murexide = 1 10 m*M*.

Equal volumes of murexide solution and HCl of desired strength were mixed, and the absorption of the mixture at $\lambda = 530$ mμ was recorded at different intervals of time. It was interesting to note that the absorption decreased progressively and permanently with time (Fig. 1) ; this was accompanied by gradual disappearance of the reddish pink colour, characteristic of murexide. The data in Fig. 1 further show that smaller the concentration of HCl,

the slower is the decrease in the absorption. Thus e.g., the time necessary for a decrease to half of the initial value of the optical density was 2.9, 3.4 and 7 mins. with 10, 6.25 and 2.5 mM of HCl.

The results obtained for the decomposition of half of the initial amounts of murexide with a fixed acid concentration showed that the reaction was essentially of first order (Table I).

TABLE I

p_H	Molar conc. of murexide $C_1 \times 10^3$.	$C_2 \times 10^3$.	$t^1_{\frac{1}{2}}$	$t^2_{\frac{1}{2}}$	n.
2.2	0.125	0.0625	4.25	3.825	0.96
2.4	0.125	0.0625	6.625	5.125	0.93
2.6	0.125	0.0625	8.25	7.00	0.96
2.6	0.100	0.0500	4.30	3.20	0.93
2.6	0.075	0.0375	3.60	3.05	0.96
2.6	0.050	0.0250	3.20	3.00	0.98
2.8	0.125	0.0625	17.00	12.00	0.91
				Mean	0.95

TABLE II

Variation of the first order rate constant with the concentration of the hydrochloric acid.

Murexide concentration = 0.10 mM.

Molar conc. of HCl ($C \times 10^3$).	Approx. p_H of the mixed soln.	$k_1 \times 10^5$.	Molar conc. of HCl ($C \times 10^3$).	Approx. p_H of the mixed soln.	$k_1 \times 10^5$.
10.0	2.15	22.7	5.0	2.45	13.2
8.75	2.20	22.4	4.25	2.55	10.8
8.25	2.25	21.2	3.75	2.60	8.8
7.50	2.30	18.9	2.50	2.70	6.3
6.25	2.35	12.3	1.00	3.15	1.3

The first order rate constant, k_1, can be calculated from the following equation relating the readings (r of optical density with time t

$$\log (r' - r) = a - k_1 t$$

when r' is the reading at time $t + T$, where T is a suitably chosen constant interval of time. Plots of $\log (r' - r)$ against t gave straight lines. The values of k_1, computed from the slope of these lines, are shown in Table II. k_1 increased sensibly linearly with the concentration (C) of HCl ; it appeared to obey the following relationship up to a concentration of 0.01 M of HCl (temperature 25°) :

$$k_1/\text{min}^{-1} = 2.56 \times 10^{-3} C.$$

Author's grateful thanks are due to Prof. K.S G. Doss, Director, Indian Institute of Sugar Technology, for his interest in the work.

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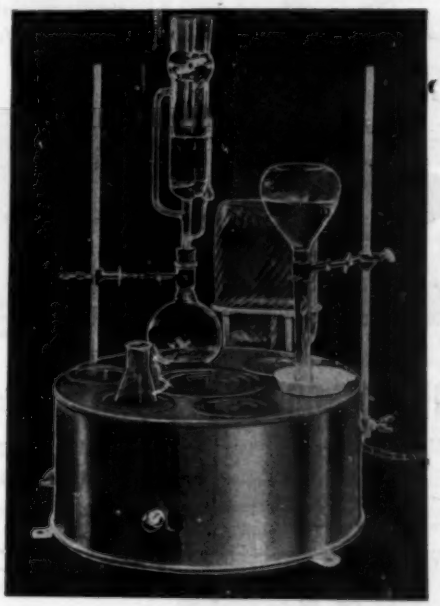

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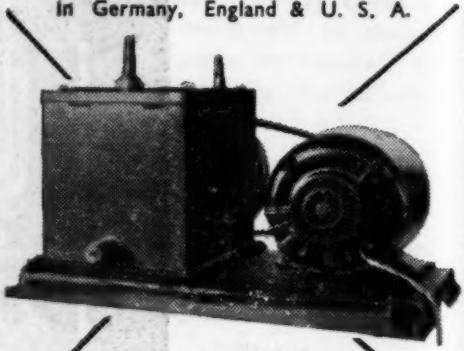

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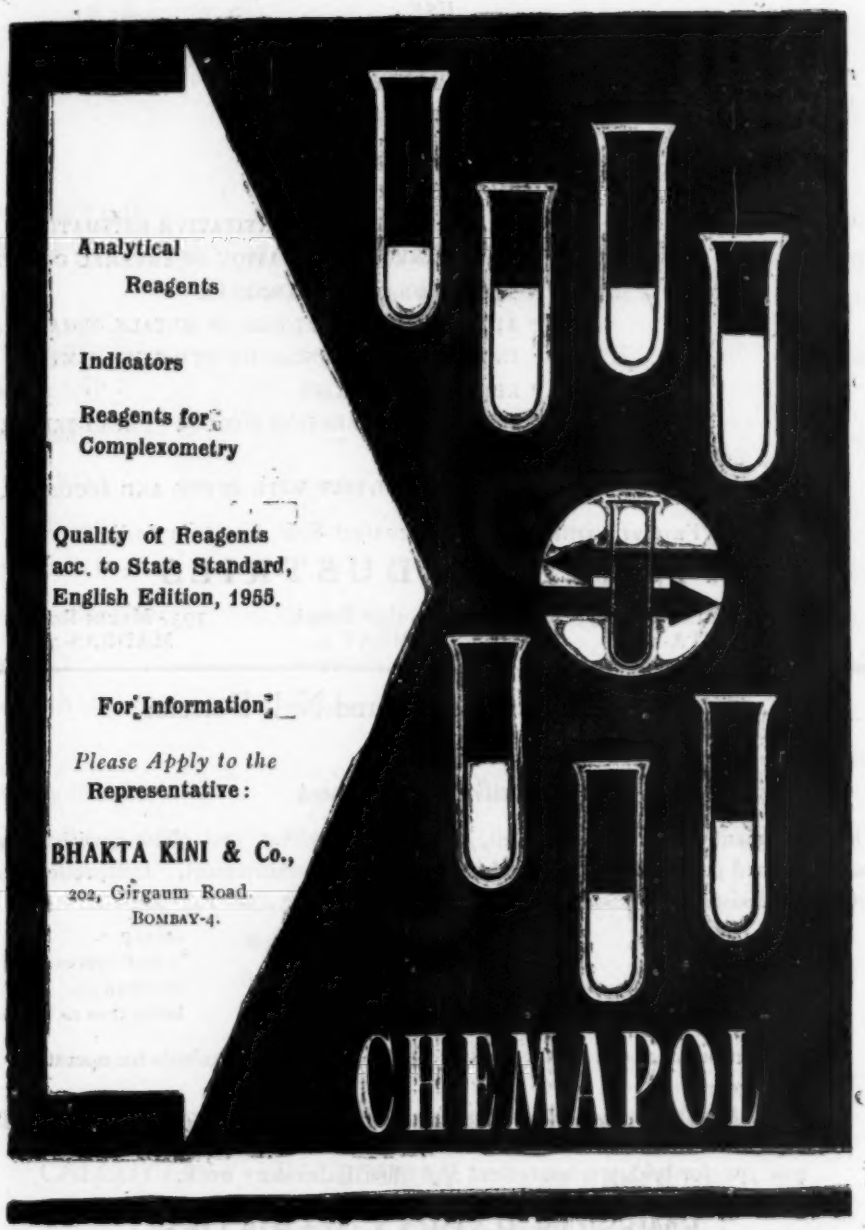

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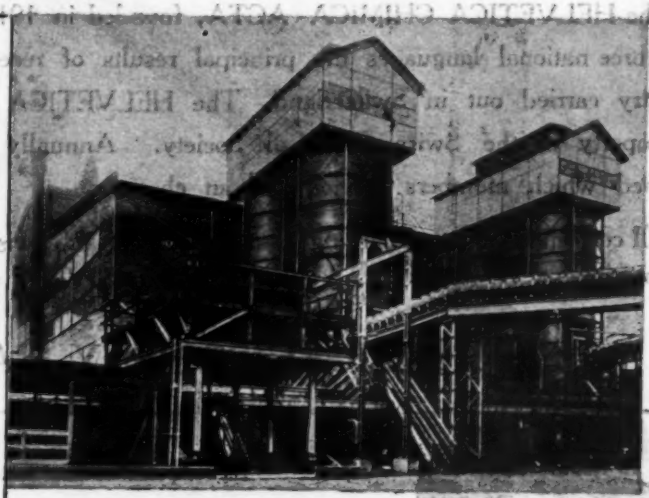

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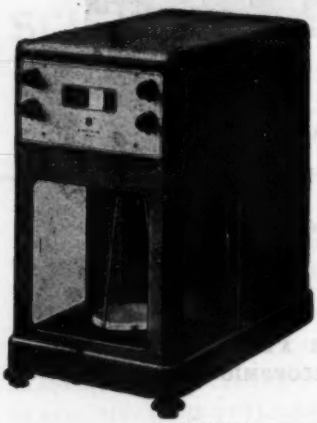

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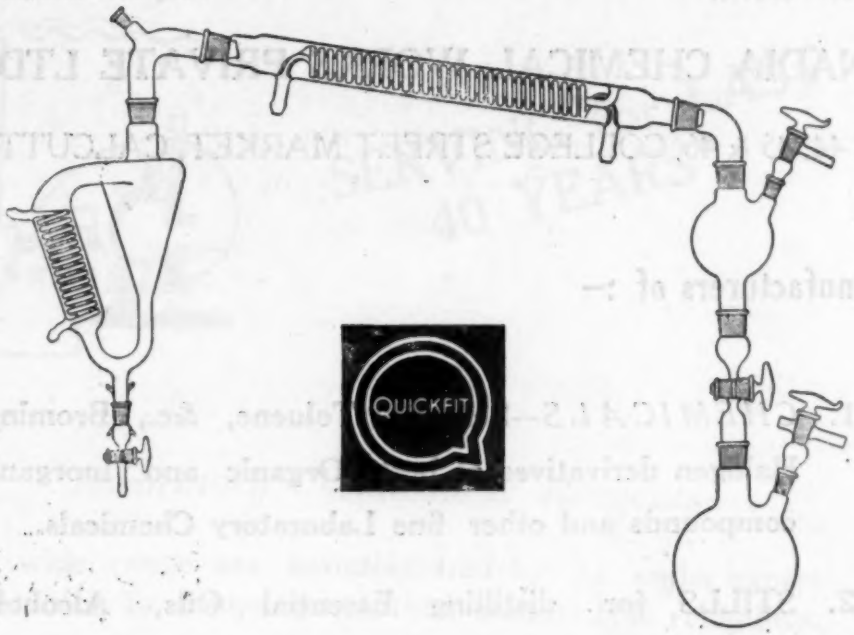

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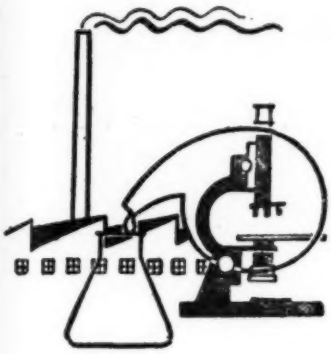

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Further details can be had from

SOLE AGENTS:

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